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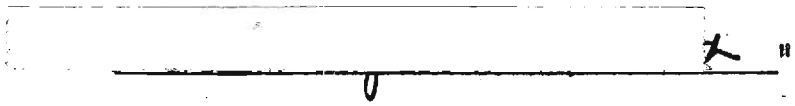

ISOTHERMAL CHANGES IN ENTHALPY FROM JOULE-THOMSON MEASUREMENTS

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A THESIS

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Master of Science in the School

of Chemical Engineering

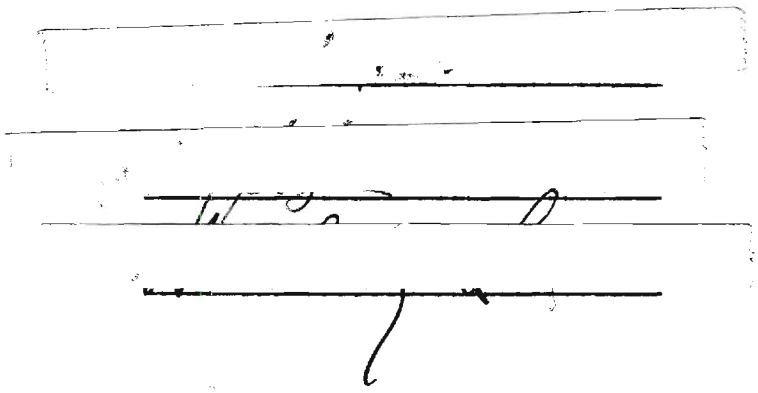
by

William Capell Duckworth

June 1954

ISOTHERMAL CHANGES IN ENTHALPY
FROM JOULE-THOMSON MEASUREMENTS

Approved



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LIST OF ILLUSTRATIONS

Table 1. Symbols Used in the Thesis

μ	Joule-Thomson coefficient, $(\partial T/\partial P)_H$
μ^o	Joule-Thomson coefficient at zero pressure
μ_f	Joule-Thomson coefficient taken graphically near the lowest temperature and pressure recorded for an isenthalp
μ_{avg}	Joule-Thomson coefficient calculated by dividing the difference between successive temperatures by the difference between successive pressures
C_p	Specific heat at constant pressure
C_p^o	Specific heat at zero pressure
H	Enthalpy
H^o	Enthalpy at zero pressure
T	Temperature
T_c	Critical Temperature
T_R	Reduced temperature (= T/T_c)
T_o	Temperature of an isenthalp at zero pressure
T_f	Lowest temperature recorded for an isenthalp
P	Pressure
P_c	Critical pressure
P_R	Reduced pressure (= P/P_c)
P_f	Lowest pressure recorded for an isenthalp
P_s	Standard pressure
V	Volume
V_s	Standard Volume
B	Second virial coefficient in equation of state $V = RT/P + B$
α, β, γ	Constants of specific heat equation

Table 1. Symbols Used in the Thesis (cont'd)

n	Exponent of function (T_{c_i}/T_{c_w}) in enthalpy correlation formula
c	Compressibility factor (PV = cRT)
λ	Activity coefficient
τ	$\frac{1}{T}$

ISOTHERMAL CHANGES IN ENTHALPY FROM JOULE-THOMSON MEASUREMENTS

ABSTRACT

Adiabatic expansion of a substance, in the absence of any useful work, takes place at constant enthalpy. For an ideal gas, the expansion would also take place at constant temperature, but, for any real substance, the expansion is accompanied by a change in temperature. The differential coefficient $(\partial T/\partial P)_H$, the symbol for which is μ, is called the Joule-Thomson coefficient, after the two men who first investigated the effect. The fundamental equation for this effect is

$$\mu C_p = -\left(\frac{\partial H}{\partial P}\right)_T \qquad (1)$$

By means of a well-known thermodynamic relation, equation (1) may also be written in the following form:

$$\mu C_p = T\left(\frac{\partial V}{\partial T}\right)_P - V$$

When P = 0, equation (2) can be expressed in the form

$$\mu^\circ C_p^\circ = T\left(\frac{dB}{dT}\right) - B \qquad (3)$$

where B is the second virial coefficient in the equation of state for the substance, and is a function of temperature only.

The primary purpose of the thesis was to determine, for several gases, the change in enthalpy with pressure, at constant temperature, by combining known Joule-Thomson measurements (in the form of P-T data along isenthalps) with C_p° data of other investigators. A secondary

purpose of the work was to examine the quantity $(H^{\circ}-H_P)_T/T_c$ as a function of reduced temperature T_R, and reduced pressure, P_R, at temperatures below the critical temperature, and to obtain, if possible, a correlation in this temperature and pressure range. Such a correlation has been fitted to experimental enthalpy data for several substances by York and Weber (1), in the range above the critical temperature.

The Joule-Thomson measurements given in the literature have been examined, and those data which make it possible to draw isenthalps in the P-T plane, extending below the critical temperature in the vapor phase, have been used. The enthalpy difference between isenthalps has been identified from the relation

$$(H^{\circ}-H_P)_{T_f} = \mu^{\circ}C_p^{\circ} P_f$$

where $\mu^{\circ}C_p^{\circ}$ is determined from equation (3) at T_f and P_f, and where P_f and T_f correspond to the lowest pressure and temperature reported on the particular isenthalp under consideration.

It is apparent from equation (4) that calculation of the quantity $(H^{\circ}-H_P)_{T_f}$ requires P-T data for isenthalps, the second virial coefficient as a function of temperature, and C_p° as a function of temperature. The C_p° data were taken from the best available sources in the literature. Since, in principle, the second virial coefficient can be calculated from the Joule-Thomson data, an attempt was made to calculate it in this way. The attempt was unsuccessful, because the P-T data available were not accurate enough, or did not extend to low enough pressure. For this reason, second virial coefficients were taken from work already in the literature.

Since H^o is a function of T only, once the quantity $(H^o-H_P)_{T_f}$ was determined, the enthalpy of the isenthalp could be determined by setting $H^o_o \equiv 0$:

$$\int C^o_p \, dT = H^o - H^o_o \equiv H^o \tag{5}$$

$$H^o - (H^o-H_P)_{T_f} = (H_P)_{T_f} \tag{6}$$

where $(H_P)_{T_f}$ is the enthalpy of the isenthalp. The zero pressure enthalpy can be calculated from temperatures read at different pressures along the isenthalp. Since the enthalpy of the isenthalp is constant, values of $(H^o-H_P)_T$ can be calculated for the pressures at which the temperature is read.

In this way, the quantity $(H^o-H_P)_T/T_c$ was calculated over a range of reduced temperature from 0.80 to 1.20, and over a range of reduced pressure from 0.10 to 1.25, from the two substances, carbon dioxide and nitrogen. Data on other substances, extending below the critical temperature in the vapor region, were either unavailable, or scanty. The enthalpy data on water were available, and it was known that Joule-Thomson measurements had been used in calculating these enthalpy data. For these reasons, the enthalpy data on water were included in the present correlation study. A correlation was obtained by plotting the quantity $(H^o-H_P)_T/\phi T_c$ against P_R, with T_R as parameter. In this correlation, $\phi = \left(T_{c_i}/T_{c_w}\right)^n$, where T_{c_i} is the critical temperature of the substance under consideration, and T_{c_w} is the critical temperature of water, and n is assumed to be a function of reduced temperature only.

The values of $(H^o-H_P)_T/T_c$, calculated by means of this correlation, give results which are in better agreement with observed data for H_2O,

CO_2, and N_2, than correlation given by Watson and Smith (2), by Hougen and Watson (3), or by Hougen and Watson as corrected by the ϕ-function of York and Weber (1), in the range where the correlations can be compared. Values of $(H^o-H_p)_T/T_c$ for benzene and n-pentane have also been calculated from Joule-Thomson data and these have been compared with the values predicted by our correlation, and by other correlations mentioned above. Our correlation compares favorably with these others.

We conclude that our method for determining the effect of isothermal changes in pressure on enthalpy from isenthalps in the P-T plane is a satisfactory one, and that our correlation of the quantity $(H^o-H_p)_T/T_c$ with reduced temperature and pressure, although based on a small amount of data, covers with some accuracy a range of reduced temperature and pressure below the critical temperature, a range over which this quantity had not been examined previously.

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(1) York, Robert and Harold G. Weber, "Isothermal Changes in Enthalpy for Some Gases," Industrial and Engineering Chemistry, 32 (1940), 388-392.

(2) Watson, K. M. and E. F. Nelson, "Improved Methods for Approximating Critical and Thermal Properties of Petroleum Fractions," Industrial and Engineering Chemistry, 25 (1933), 880-887.

(3) Hougen, O. A. and K. M. Watson, Chemical Process Principles: Part Two; Thermodynamics. New York: John Wiley and Sons, Inc., 1947, p. 495.

ISOTHERMAL CHANGES IN ENTHALPY FROM JOULE-THOMSON MEASUREMENTS

CHAPTER I

INTRODUCTION

Description of the Joule-Thomson Experiment.--In the Joule-Thomson experiment, a substance is expanded adiabatically without doing any useful work. The enthalpy of the substance remains constant, and, if the substance is an ideal gas, the temperature also remains constant. For a real substance, however, the temperature changes during expansion.

In the original experiments of Joule and Thomson (1), compressed air was allowed to expand through a stopcock, and the heat effect was determined by measuring the temperature of the air on both sides of the stopcock. This method was abandoned, because it was not precise enough, and a porous material was substituted for the stopcock. These methods are still in general use. The compressed gas is expanded through either a porous plug, or a valve. The temperature and pressure are measured as the pressure is decreased, and the calculations are made from these data.

Mathematical Analysis.--The fundamental equation for the Joule-Thomson effect is

$$\mu C_p = -\left(\frac{\partial H}{\partial P}\right)_T \qquad (1)$$

where μ is the Joule-Thomson coefficient. By means of a well-known thermodynamic relation, equation (1) may also be written in the

following form:

$$\rho C_p = T \left(\frac{\partial V}{\partial T}\right)_P - V \tag{2}$$

At sufficiently low pressure

$$V = \frac{RT}{P} + B \tag{3}$$

where B is the second virial coefficient in the equation of state for the gas, and is a function of temperature only. Using this relation, equation (2) becomes

$$\rho C_p = T \left(\frac{dB}{dT}\right) - B \tag{4}$$

The purpose of this work was to determine the effect on the enthalpy of several gases of isothermal changes in pressure, and to express the quantity $(H^\circ - H_P)_{T/T_c}$ as a function of reduced temperature and reduced pressure. It was of particular interest to examine this quantity as a function of T_R and P_R in the range below the critical point, because the experimental enthalpy difference, $(H^\circ - H_P)_T$, had not been examined in this area before. The calculations of $(H^\circ - H_P)_T$ in other correlations have been based on derived quantities, such as compressibility factor (2), or activity coefficient (3).

Joule-Thomson measurements, in the form of P-T data along isenthalps, provide a means of calculating the quantity $(H^\circ - H_P)_T$ over a range of reduced temperatures and pressures. In this work, the quantity $(H^\circ - H_P)_T$ for each isenthalp is determined at T_f, the lowest reported temperature for the isenthalp, from the relation

$$-\left(\frac{\partial H}{\partial P}\right)_T = T \frac{dB}{dT} - B \tag{5}$$

which can be obtained by substituting for μC_p in equation (4) its value from equation (1). Since H^o is a function of T only, it can be calculated at T_f (provided C_p^o is known as a function of T) and the enthalpy of each isenthalp can be determined by subtracting $(H^o-H_p)_{T_f}$ from H^o. If the enthalpies of several isenthalps, covering a range of temperature and pressure, are determined, the quantity $(H^o-H_p)_T$ can be determined over this temperature and pressure range by drawing isotherms through the isenthalps. The zero pressure enthalpy can be determined from the temperature T. The enthalpy of the isenthalp having been determined as described above, the quantity $(H^o-H_p)_T$ can be calculated.

This method of calculating isothermal enthalpy differences has been used by Keyes (4), who used the method to calculate the second virial coefficient of nitrogen from the Joule-Thomson data of Roebuck and Osterberg (5) by means of the relation

$$-\mu^o C_p^o = \frac{d(B\tau)}{d\tau} \qquad (6)$$

where $\tau = \frac{1}{T}$, and the superscript zero indicates that the quantity is to be determined at zero pressure. Keyes did not state how he calculated μ^o, but presumably he either determined it from the Joule-Thomson data of Roebuck and Osterberg, or used for μ^o the value of μ at one atmosphere, which Roebuck and Osterberg reported.

Review of the Literature.--Johnston (6) has reviewed the experimental data on the Joule-Thomson effect, and his review has been used in locating data for the Joule-Thomson effect published prior to 1948. Only Brilliantinov (7) has reported experimental results since that time. Calculated values for μ have been reported by de Groot and Michels on CO_2 (8), by Lunbeck, et al., on N_2 (9), and by Deming and Deming on N_2 (10). These

values are compared with the experimental results of Roebuck, et al., on these two gases (table 22, for CO_2, and table 33, for N_2). Other calculated values of μ were not pertinent to the present work.

Nature of the Data Reported by Various Investigators.--For the purposes of our calculations, the form in which the Joule-Thomson data were reported was very important. Since we wished to determine the effect of changes in pressure at constant temperature on the quantity $(H^o-H_p)_T$ in the region below T_c by drawing isotherms across isenthalps in the P-T plane, it was necessary to have P-T data along isenthalps. Furthermore, since we wished to use an equation of state in the virial form, with two virial coefficients, it was necessary to have P-T data given to a pressure of a few atmospheres. An equation of state with two virial coefficients is valid only if the pressure is sufficiently low. It was desirable that some of the P-T curves lie below the critical temperature, because this was the range in which we were particularly interested. The method chosen for identifying the isenthalps required that the P-T curve end in the vapor region, and, if any calculations were to be based on an isenthalp, a large part of it must lie in the vapor region. These restrictions prevented us from using most of the Joule-Thomson data available in the literature. The only data which meets these requirements is that of Roebuck and co-workers on CO_2 (11), and N_2 (5). Only a few of the isenthalps reported in these articles meet the requirements.

In correlating $(H^o-H_p)_T/T_c$ with T_R and P_R, the thermodynamic data of Keenan and Keyes on water (12) were used in addition to the data for CO_2 and N_2. Joule-Thomson measurements had been used extensively in calculating these data for water, and this fact partly justifies our use in

this thesis of enthalpies taken from the steam tables of Keenan and Keyes.

The data of Brown and co-workers on benzene (13), and n-pentane (14), gave us scattered values of $(H^{o}-H_{p})_{T}$ for those substances, and these were used as independent checks of our correlation.

A large amount of experimental Joule-Thomson data for hydrocarbons has been reported by Sage, Lacey, and co-workers (15, 16, 17, 18, 19, 20, 21, 22). These investigators tabulate μ as a function of temperature and pressure, and they have calculated from these data the enthalpy of various hydrocarbons as a function of pressure and temperature. In general, the temperature range of these measurements extends below the critical temperature.

Collins and Keyes have reported some measurements of the Joule-Thomson effect for steam (23), as well as for some other substances. They used the "isothermal" system, in which gas is expanded, then heated to its original temperature on the low pressure side of the apparatus. In this way, the heat effect, which in our work is calculated from P-T data, is measured directly.

CHAPTER II

IDENTIFICATION OF ISENTHALPS

The Various Methods Considered.--We wished to determine the enthalpy difference between isenthalps by extrapolating the P-T curve to zero pressure. At zero pressure the enthalpy, H°, is a function of temperature only, and data for the calculation of H° for the gases considered are available. Using Joule-Thomson data on CO_2 (11), several methods were tried for making the extrapolation. These were:

(a) Calculation from equation (5), using second virial coefficient data taken from the literature;

(b) Integration of a known equation of state;

(c) Extrapolation of a graph of μ vs P;

(d) Linear extrapolation of the isenthalps;

(e) Use of a numerical method, the Lagrange formula.

Description of the Method Used in this Work.--The first method was finally adopted for the calculation. This method was used in preference to the integrated form of a known equation of state because, in the temperature range covered by the Joule-Thomson data of Roebuck and co-workers on CO_2 and N_2, the constants had not been determined for the equations of state which we integrated. In principle, the second virial coefficient can be determined by substituting P-T data along isenthalps into an integrated equation of state. We attempted to make the calculation in this way, but the second virial coefficient so calculated was in error (see Appendix G,

where the integration is discussed, and table 48*, where values calculated for the constants of the Beattie-Bridgeman equation of state are given). We preferred method (a) to method (c), because the latter would have required extrapolation of μ, and we found that values of μ calculated from equations of state were not very accurate. Linear extrapolation to zero pressure, or extrapolation by use of the Lagrange formula, probably would not lead to serious error when T_f is much greater than T_c, but it leads to large errors when T_R is near, or below, 1.0. This was the temperature range in which we were interested. Some values of T_o (the temperature of the isenthalp at zero pressure) calculated by the use of the integrated form of the Beattie-Bridgeman equation of state, obtained by linear extrapolation of the isenthalp, and obtained by use of the Lagrange formula, are given in the Appendix, (table 49).

The method chosen for the identification of the isenthalps depends on the fact that the zero pressure Joule-Thomson coefficient, μ^o, and the zero pressure specific heat, C_p^o, are functions of temperature only. Therefore, when P = 0, equation (1) becomes

$$\mu^o C_p^o = -(\partial H/\partial P)_T \qquad (7)$$

and, when T is constant,

$$-dH = \mu^o C_p^o dP \qquad (8)$$

which can be integrated between the final recorded pressure, P_f, and P = 0,

*Tables 22-50 are given in the Appendix.

to give

$$(H^{\circ}-H_P)_{T_f} = \mu^{\circ} C_p^{\circ} P_f \qquad (9)$$

where T_f is the temperature at P_f, and μ° and C_p° are taken at T_f.

From (5) and (7),

$$\mu^{\circ} C_p^{\circ} = T_f(dB/dT) - B \qquad (10)$$

where μ°, C_p°, dB/dT, and B are taken at T_f. Using equation (9) and equation (10),

$$(H^{\circ}-H_P)_{T_f} = (T_f(dB/dT)-B)P_f \qquad (11)$$

Equation (11) gives the difference between the zero pressure enthalpy at T_f, and the enthalpy of the isenthalp at T_f and P_f. For the calculation of $(H^{\circ}-H_P)_T$ from this equation, values of B, taken from the literature, were plotted against T. To solve the equation, B was taken from this graph, or interpolated from tabulated values by means of a numerical method, while the slope dB/dT was obtained from the tabulated values by the method of Newton or Douglass-Avakian.

The zero pressure enthalpy, $H^{\circ}-H_o^{\circ}$, can be calculated from C_p°. Values of C_p° have been taken from the literature, and fitted to an equation of the form

$$C_p^{\circ} = \alpha + \beta T + \gamma T^2 \qquad (12)$$

where α, β, and γ are constants. This equation can be integrated to give $H^{\circ}-H_o^{\circ}$:

$$H^{\circ}-H_o^{\circ} = \alpha T + \frac{\beta}{2} T^2 + \frac{\gamma}{3} T^3 \qquad (13)$$

In this work, $H^{\circ}_{o} \equiv 0$ when $T = 0^{\circ}K$, so substitution of T_f into equation (13) gives H° at T_f. This can be combined with equation (11) to give H_P, the enthalpy of the isenthalp:

$$H^{\circ}_{T_f} - (H^{\circ} - H_P)_{T_f} = (H_P)_{T_f} \qquad (14)$$

CHAPTER III

DATA USED IN THE CALCULATIONS

Joule-Thomson Data.--Roebuck and co-workers have reported data on the Joule-Thomson effect for CO_2 (11), N_2 (5), air (24), He and air (25), He (25), A (26), He and N_2 mixtures (27), and mixtures of He and A (28). We did not want to use mixtures, and we did not want to use He, because its critical temperature is so low. Roebuck reported some data on A below the critical, but he reported that his porous plug clogged on those runs. Carbon dioxide and nitrogen were the only substances for which we were able to find extensive data below the critical temperature. Roebuck gave P-T data for forty curves for CO_2. However, only seven curves below the critical could be used, for reasons discussed in Chapter I. For nitrogen, only four curves below the critical could be used. A total of nine sets of P-T data were used for CO_2 (table 3), and ten for N_2 (table 7). This made it possible to calculate the enthalpy differences over the approximate range P_R = 0.10-2.50 for both substances. The temperature ranges covered were T_R = 0.80-2.50 for N_2, and 0.80-1.60 for CO_2.

Enthalpy differences which we calculated from the Joule-Thomson data of Lindsay and Brown on benzene (13) (table 18), and of Pattee and Brown on n-pentane (14) (table 19) have been used to furnish independent checks of our correlation. These investigators reported only an initial high pressure, and final low pressure, with corresponding temperatures.

Consequently, these data furnish only scattered points below the critical point.

Second Virial Coefficient Data.--The second virial coefficient of CO_2 has been reported by Schäfer (29) for the range 203-273°K. We calculated the second virial coefficient from 298-423°K from the P-V-T data of Michels and de Groot (30). These two sets of values of B were plotted against T, and a smooth curve was drawn, from which values of B were tabulated at 5° intervals of T (table 4, and fig. 1).

Bloomer and Rao (31) published compressibility data on N_2, based in part on unpublished data of Friedman, White, and Johnston (32). These latter workers reported the second virial coefficient to 80°K*, and a graph of B vs. T is included in the work of Bloomer and Rao. Bloomer and Rao reported compressibility data, in this temperature range, to a pressure of 10 psia. We calculated the value of B from these data. The constants of the Beattie-Bridgeman equation for nitrogen have been reported for the range 124-673°K (33). Keyes derived two equations for the second virial coefficient of nitrogen (34). These are:

$$B_o T^{\frac{1}{4}} = (10.08 - 766.155\,\tau^{\frac{3}{4}} - 1.7545 \cdot 10^8\,\tau^{\frac{15}{4}}) \quad cc/g \qquad (15)$$

$$B_o T^{\frac{1}{4}} = (10.08 - 767.33\,\tau^{\frac{3}{4}} - 1.812 \cdot 10^8\,\tau^{\frac{15}{4}}) \quad cc/g \qquad (16)$$

Equation (15) was derived to fit most of the measurements of the second virial coefficient available to Keyes in 1941. Equation (16) was derived to fit the values of the second virial coefficient obtained by Keyes from the Joule-Thomson data of Roebuck and Osterberg. Values obtained from

*The method by which the second virial coefficient was obtained is not described.

equation (16) are about 0.2% higher than those obtained from equation (15). Both equations cover the approximate range, 123-673°K.

Benedict has made some P-V-T measurements below the critical point for nitrogen (35), but these measurements are in the liquid region.

Gratch has reviewed the compressibility data on nitrogen available in 1948 (36).

Values of B, obtained from the sources described above, have been plotted against T, and a smooth curve drawn, from which values of B were tabulated at 5° intervals of T (fig. 2, and table 8).

The second virial coefficient of benzene has not been recorded in the temperature range for which Brown and Lindsay reported Joule-Thomson data. Enthalpy differences for benzene were determined by drawing a line through the initial and final points, and continuing the line to P = 0. This was the method of Lindsay and Brown. They state that the isenthalps are straight lines within experimental error. Our calculations of enthalpy differences probably are more accurate than those given in the earlier work, because C_p^o data available to us are much more accurate than those available to Brown and Lindsay in 1935.

No attempt was made to find data for the second virial coefficient of $n\text{-}C_5H_{12}$. A straight line was drawn through the initial and final points, extended to zero pressure, and the enthalpy differences calculated from C_p^o data.

Specific Heat Data.--Specific heat data for N_2 have been given by Goff and Gratch (37) (table 9), for CO_2 by Wooley (38) (table 6), and for H_2O by Keyes (39). In the first two cases, these data were fitted to a three constant equation in T, over the required range, and these

equations were integrated to get H^o (table 5). For steam, an equation for H^o was given by Keyes (39) (table 5). Rossini, et al., have reported C_p^o for n-pentane (40) (table 47), and for benzene (41) (table 44). The latter data have been corrected by Scott, and the corrections have been reported by Organick and Studhalter (42).

Critical point data, and certain other constants used in the thesis, are listed in table 2.

These data completed the information required for the calculations.

Table 2. Physical Constants Used in This Work

(a) Critical Point Data

Substance	T_c, °K	P_c, Atm.	Reference
CO_2	304.19	72.9	43
N_2	126.26	33.54	44
H_2O	647.27	218.16	12
C_6H_6	562.09	48.34	45
$n\text{-}C_5H_{12}$	470.3	33.0	46

(b) Molecular Weights Used

Substance	Molecular Weight
CO_2	44.010
N_2	28.016
H_2O	18.016
C_6H_6	78.108
$n\text{-}C_5H_{12}$	72.146

(c) Some Other Constants

$0^\circ C = 273.16^\circ K$*

1 I.T. calorie = 1.000652 defined calorie

$$1 \frac{\text{g-calorie}}{\text{g-mole-}^\circ K} = 41.2930 \frac{\text{cc-atm}}{\text{g-mole-}^\circ K}$$

$R = 0.08206$ l-atm/g-mole-°K
$= 1.98719$ g-mole/g-cal-°K

1 int. joule/g = 4.303822 I.T. cal/g-mole for H_2O
1 BTU/lb = 10.008666 I.T. cal/g-mole for H_2O
1 int. joule/g = 4.306557 defined cal/g-mole for H_2O
1 cal = 4.1833 int. joule

The Defined Calorie is Used Throughout the Work

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*In the calculations on CO_2, $0^\circ C = 273.15^\circ K$. This value was used by Michels.

Table 3. Joule-Thomson Data of Roebuck, et al., on CO_2* (11)

Isenthalp I-4	
P, Atm.	T, °C.
3.8	128.90
19.5	137.19
43.5	148.78
64.8	158.08
88.4	167.62
113.1	176.65
135.5	183.46
156.2	190.33
194.7	200.48

Isenthalp I-6	
P, Atm.	T, °C.
4.6	47.04
19.5	60.77
43.2	79.25
66.6	94.95
90.5	108.35
112.5	119.45
134.8	129.09
155.5	136.59
194.7	149.49

Isenthalp I-8	
P, Atm.	T, °C.
2.5	- 0.94
24.7	+25.78
46.2	47.26
70.4	67.24
93.2	122.60
193.5	125.09

Isenthalp I-9	
P, Atm.	T, °C.
1.9	-61.60
22.5	-15.30
41.1	+ 8.22
64.4	34.05
86.2	52.66
110.8	68.22
132.2	78.91
155.0	88.15
193.5	100.03

Isenthalp II-1	
P, Atm.	T, °C.
1.9	-41.17
8.4	-28.18
14.5	-17.30
20.2	- 7.30
30.0	+ 6.49
39.7	18.94
49.4	30.03
59.0	40.00

Isenthalp II-5	
P, Atm.	T, °C.
1.9	-52.63
3.8	-47.48
5.9	-42.94
13.1	-28.23
17.6	-19.69
22.0	-12.09
27.9	- 2.86
36.0	+ 8.56
46.1	21.11
55.4	31.38
63.9	40.00

Isenthalp II-6	
P, Atm.	T, °C.
2.0	-62.63
15.9	-26.61
20.0	-19.32
28.9	- 6.50
36.1	+ 2.32
44.9	14.09
68.7	40.00

Isenthalp II-9	
P, Atm.	T, °C.
1.6	-57.30
4.0	-50.71
5.6	-47.16
9.6	-39.26
14.4	-29.26
19.7	-19.15
24.2	-10.97
28.7	- 3.82
38.0	+ 9.36
47.6	21.11
56.7	31.22
65.5	40.00

Isenthalp II-10	
P, Atm.	T. °C
1.5	-64.51
5.8	-53.53
8.9	-43.16
12.2	-33.77
40.6	+ 8.95
50.3	20.79
58.2	29.25
68.7	40.00

*The numerals identifying the isenthalps are our own.

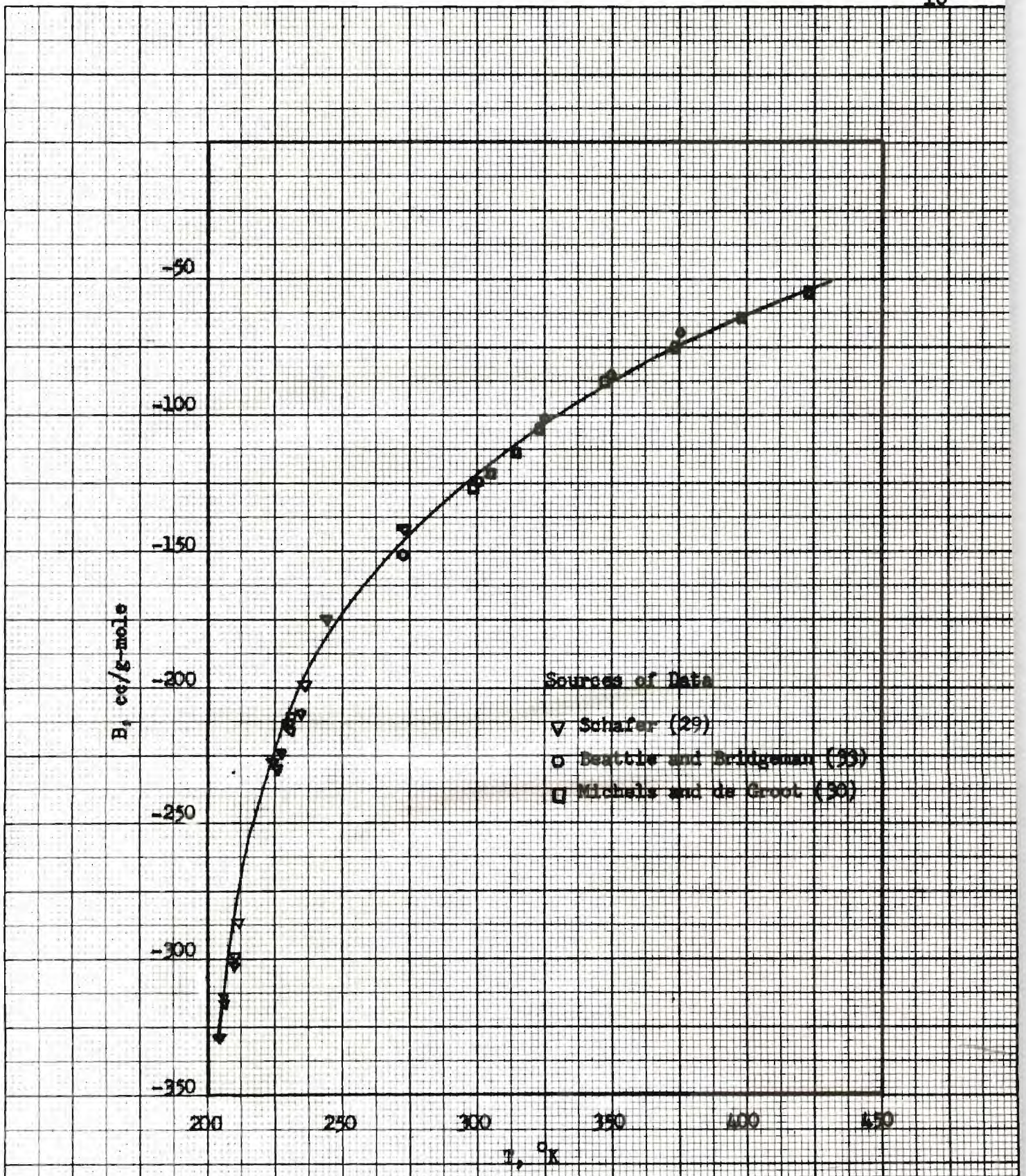

Fig. 1 The Second Virial Coefficient of CO_2

Table 4. The Second Virial Coefficient of CO_2

Values Read from Smooth Curve in Fig. 1

T, °K	B, cc/g mole	T, °K	B, cc/g-mole
205	-316	320	-106
210	-290	325	-103
215	-266	330	-100
220	-244	335	- 97
225	-222	340	- 94
230	-210	345	- 91
235	-198	350	- 88
240	-188	355	- 85
245	-180	360	- 83
250	-172	365	- 80
255	-166	370	- 78
260	-160	375	- 75
265	-154	380	- 73
270	-149	385	- 71
275	-144	390	- 68
280	-139	395	- 66
285	-134	400	- 64
290	-129	405	- 62
295	-125	410	- 59
300	-121	415	- 57
305	-117	420	- 55
310	-113	425	- 53
315	-109	430	- 51

Table 5. Equations for C_p^o and H^o for CO_2, N_2, H_2O C_6H_6, and n-C_5H_{12}

(a) Equations for C_p^o

Substance	Range, ^oK	Equation*	Ref.	Equation Number	Average Deviation
CO_2	180-600	$204.662 + 0.645558T + 3.507088 \times 10^{-4}T^2$	(38)	17	0.11%
N_2	70-400	$6.954131 - 7.6151 \times 10^{-5}T + 3.2725 \times 10^{-7}T^2$	(37)	18	0.025%
C_6H_6	300-700	$-8.06 + 0.10812T - 0.5104 \times 10^{-4}T^2$	(41, 42)	19	0.17%
n-C_5H_{12}	298.16-600	$3.65 + 0.09535T - 0.305 \times 10^{-4}T^2$	(40)	20	0.15%

(b) Equations for H^o

CO_2	180-600	$4.95615T + 7.816513 \times 10^{-3}T^2 - 2.830957 \times 10^{-6}T^3$		21	
N_2	70-400	$6.954131T - 3.80755 \times 10^{-5}T^2 + 1.09083 \times 10^{-7}T^3$		22	
C_6H_6	300-700	$-8.06T + 0.05406T^2 - 0.17013 \times 10^{-4}T^3$		23	
n-C_5H_{12}	298.16-600	$3.65T + 0.047675T^2 - 0.1017 \times 10^{-4}T^3$		24	
H_2O**	298.16-1500	$1.4722 (T-T_o) + 3.8863 \times 10^{-4}(T^2-T_o^2) + 110.16 \log \frac{T}{T} - 9.49 \times 10^{-9}(T^3-T_o^3) + 2501.09$		25	

*Units are $\frac{cal}{g\text{-mole-}^oK}$ for C_p^o, except for CO_2, the units for which are $\frac{cc\text{-atm}}{g\text{-mole-}^oK}$. Units for H^o are $\frac{cal}{g\text{-mole}}$, except for H_2O, the units for which are $\frac{joules}{gram}$.

**In this equation, T_o = ice point = 273.16 ^oK.

Table 6. Zero Pressure Specific Heat of CO_2 (38)

T, °K	$\frac{C_p^o}{R}$
190	3.826
200	3.883
210	3.941
220	4.000
230	4.059
240	4.119
250	4.178
260	4.237
270	4.295
280	4.352
290	4.409
300	4.464
310	4.519
320	4.572
330	4.624
340	4.675
350	4.725
360	4.773
370	4.821
380	4.867
390	4.913
400	4.957
410	5.001
420	5.043
430	5.085
440	5.126
450	5.166

Table 7. Joule-Thomson Data of Roebuck and Osterberg on N_2 (5)

(Pressures have to be corrected by multiplying by 0.9677) (11)

1

P, Atm.	P Corrected	T, °C.
1.5	1.45	-173.46
16.5	16.0	-150.00
44.6	43.2	-128.32
68.2	66.0	-115.62
91.8	88.8	-107.25
116.0	112.3	-101.22
136.8	132.4	- 97.47
159.5	154.3	- 94.49
181.4	175.5	- 91.63
201.8	195.3	- 91.09

2

P. Atm.	P Corrected	T, °C.
1.6	1.548	-186.18
12.9	12.5	-165.87
20.8	20.1	-155.62
26.5	25.6	-149.06
32.4	31.4	-143.17
45.3	43.8	-133.00
68.1	65.9	-120.77
92.9	89.9	-112.28
114.3	110.6	-103.25
137.5	133.0	- 97.377

3

P, Atm.	P Corrected	T, °C.
1.7	1.645	-189.81
13.2	12.8	-165.13
20.8	20.1	-157.03
25.8	25.0	-151.16
31.9	30.9	-144.82
44.5	43.1	-134.43
68.9	66.7	-121.50
91.5	88.5	-113.72
115.2	111.5	-108.39
138.2	133.7	-104.70
201.6	195.1	- 99.06

5

P, Atm.	P Corrected	T, °C.
1.5	1.45	-191.76
19.4	18.8	-158.55
40.1	39.8	-139.49
70.4	68.0	-121.74
99.8	96.5	-112.40
119.6	115.7	-108.74
141.3	136.8	-105.56
168.7	163.1	-102.64
201.8	195.0	-100.51

7

P, Atm.	P Corrected	T, °C.
2.7	2.6	24.04
19.0	18.4	27.36
42.8	41.4	31.76
65.5	63.4	35.57
89.7	86.8	38.96
111.1	107.5	41.46
135.0	130.6	44.27
159.7	152.8	46.33
201.6	195.1	49.78

8

P, Atm.	P Corrected	T, °C.
1.6	1.5	- 38.58
18.9	18.3	- 33.00
41.1	39.8	- 26.44
65.4	63.3	- 20.25
88.4	85.5	- 15.36
112.5	108.9	- 11.04
136.5	132.1	- 7.39
159.0	153.9	- 4.46
180.5	174.7	- 2.10
201.8	195.3	- 0.134

Table 7. Joule-Thomson Data of Roebuck and Osterberg on N_2 (cont'd) (5)

(Pressures have to be corrected by multiplying by 0.9677) (11)

9			10		
P, Atm.	P Corrected	T, °C.	P, Atm.	P Corrected	T, °C.
3.3	3.2	- 6.80	1.5	1.45	-108.91
19.0	18.4	- 2.70	14.6	14.1	-100.53
43.8	42.3	3.02	40.5	39.2	- 87.53
67.3	65.1	7.81	65.1	63.0	- 78.35
91.0	88.1	11.97	88.6	85.7	- 70.76
112.4	108.8	15.23	112.5	108.9	- 64.62
136.2	131.8	18.27	136.8	132.4	- 59.68
158.5	153.4	20.85	158.4	153.3	- 56.12
201.6	195.1	24.62	179.7	173.9	- 53.24
			201.8	195.3	- 50.94

11			12		
P, Atm.	P Corrected	T, °C.	P, Atm.	P Corrected	T, °C.
2.5	2.4	-146.27	4.6	4.5	83.11
17.9	17.3	-132.43	21.4	20.7	85.33
44.2	42.8	-113.95	45.0	43.5	88.18
70.1	67.8	-101.43	67.0	64.8	90.53
91.2	88.3	- 93.68	89.1	86.2	92.64
115.7	112.0	- 87.84	113.7	110.0	94.63
136.8	132.4	- 82.84	135.2	130.8	96.11
160.0	154.8	- 79.23	157.9	152.8	97.44
181.7	175.8	- 76.42	182.7	176.8	98.42
201.8	195.3	- 75.06	201.3	194.8	99.62

Table 8. The Second Virial Coefficient of N_2

Smooth Values from Fig. 4

$T^{\circ}K$	B, $\frac{cc}{mole}$	$T^{\circ}K$	B, $\frac{cc}{mole}$
75	-286	225	- 25
80	-255	230	- 24
85	-228	235	- 22
90	-204	240	- 20
95	-184	245	- 19
100	-166	250	- 18
105	-150	255	- 16
110	-136	260	- 14
115	-123	265	- 13
120	-113	270	- 12
125	-103	275	- 10
130	- 95	280	- 9
135	- 87	285	- 8
140	- 81	290	- 7
145	- 76	295	- 6
150	- 71	300	- 5
155	- 66	305	- 4
160	- 62	310	- 3
165	- 58	315	- 2
170	- 54	320	- 2
175	- 50	325	- 1
180	- 47	330	0
185	- 44	335	+ 1
190	- 41	340	+ 2
195	- 38	345	+ 2
200	- 35	350	+ 3
205	- 33	355	+ 4
210	- 31	360	+ 4
215	- 29	365	+ 5
220	- 27	370	+ 6

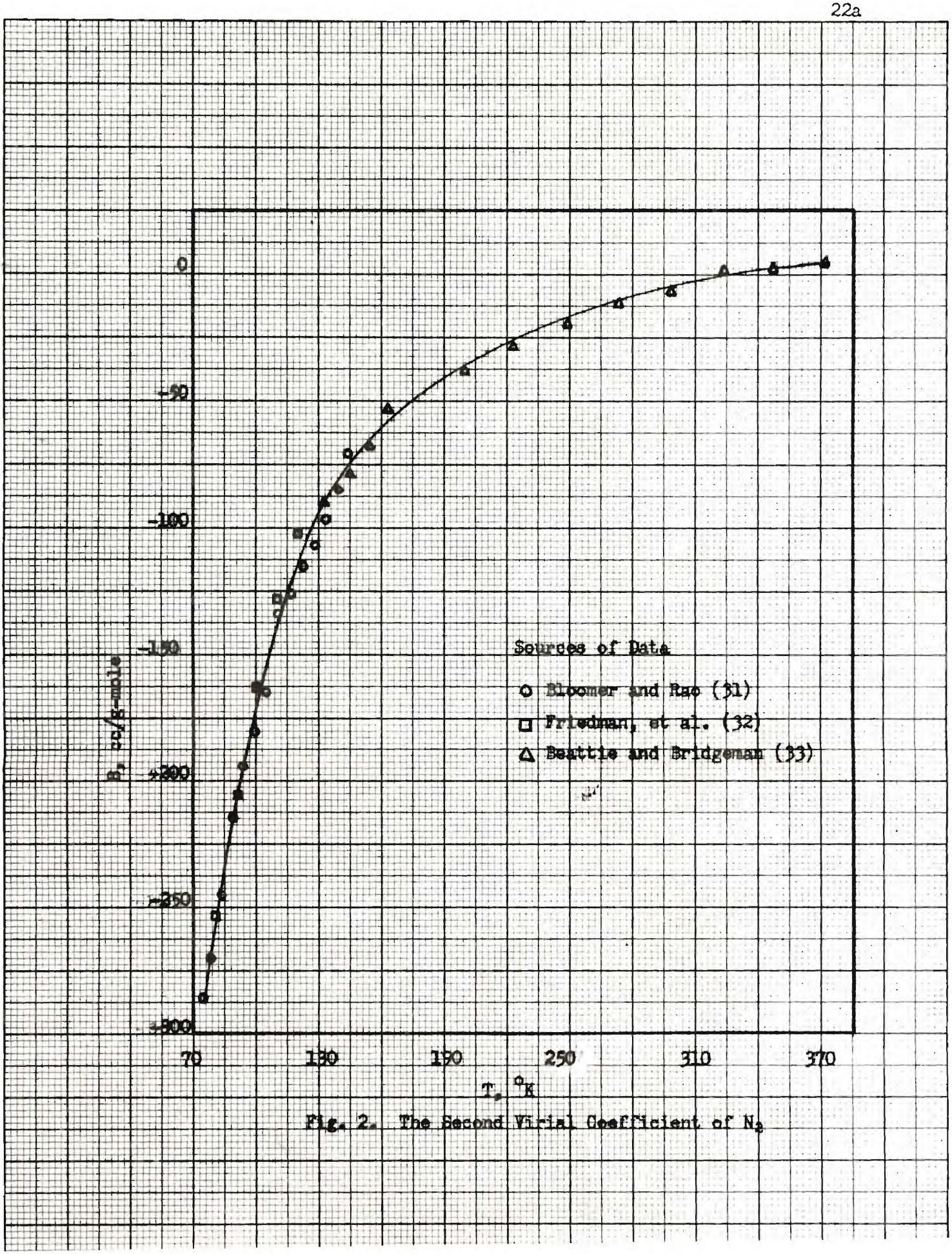

Fig. 2. The Second Virial Coefficient of N_2

Table 9. Zero Pressure Specific Heat of N_2 (37)

T, °K	C_p^o, $\frac{cal}{g\text{-}mole\text{-}°K}$	T, °K	C_p^o, $\frac{cal}{g\text{-}mole\text{-}°K}$
55.55	6.95091	200.00	6.95199
58.33	6.95092	211.11	6.95211
61.11	6.95093	222.22	6.95227
63.88	6.95095	233.33	6.95247
66.66	6.95096	244.44	6.95273
69.44	6.95097	255.55	6.95310
72.22	6.95099	266.67	6.95359
77.78	6.95103	277.78	6.95425
83.34	6.95106	305.56	6.95695
88.90	6.95110	333.33	6.96171
94.46	6.95114	361.11	6.96930
100.00	6.95118	388.88	6.98034
105.56	6.95122	416.66	6.99529
111.12	6.95126	444.44	7.01440
116.68	6.95131	472.22	7.03768
122.24	6.95135	500.00	7.06500
127.77	6.95139	527.78	7.09607
133.33	6.95143	555.56	7.13050
144.45	6.95152		
155.57	6.95161		
166.66	6.95170		
177.77	6.95179		
188.88	6.95188		

CHAPTER IV

CALCULATION OF ENTHALPY DIFFERENCES

Discussion of the Method.--From the data summarized in Chapter III, we were prepared to calculate the enthalpy differences between isenthalps on the P-T plane using equations (10) and (11):

$$(H^{\circ}-H_P)_{T_f} = \mu^{\circ}C_p^{\circ} P_f = (T_f \left(\frac{dB}{dT}\right) - B)P_f \qquad (10, 11)$$

In order to make the calculation, it was necessary to know the quantity $\frac{dB}{dT}$. From tabulated values of B and T, arranged in a table at 5° intervals (for CO_2 in table 4, and for N_2 in table 8) a difference table was made, and the formula of Newton (47) was used to obtain the derivative. Ordinarily, five terms of Newton's formula were used. Equation (11) could then be used to calculate $(H^{\circ}-H_P)_T$, the difference between the zero pressure enthalpy at the final temperature, and the enthalpy at the final temperature and pressure. Since H° could be calculated from the known temperature T_f, it was then possible to calculate the enthalpy of the isenthalp:

$$H^{\circ}_{T_f} - (H^{\circ}-H_P)_{T_f} = (H_P)_{T_f} \qquad (14)$$

As a check on the value of $\frac{dB}{dT}$, an average $\frac{\Delta B}{\Delta T}$ was calculated over the temperature range near T_f, and this was compared with the value of $\frac{dB}{dT}$ obtained from Newton's formula. Since the coefficient $\frac{dB}{dT}$ generally becomes greater as the temperature decreases, it should be greater than $\frac{\Delta B}{\Delta T}$. As a further check, the method of Douglass-Avakian (48) was used,

and all of these values were compared with the value of $\frac{dB}{dT}$ obtained graphically from the B vs. T curve at T_f (table 24 for CO_2, and table 31 for N_2). In general, the formula of Newton gave results which appeared to be more nearly correct at smaller values of T_R, while that of Douglass-Avakian gave results which appeared to be more nearly correct at higher temperatures, and these formulas were used over the corresponding ranges. It was particularly important to obtain a correct value for $\frac{dB}{dT}$ at low temperatures, because the slope is quite large there. The method of Douglass-Avakian would be in error there, because the method is based on the assumption that the function can be expressed satisfactorily in a power series, which is far from the case at lower temperatures.

After the enthalpy of each curve had been identified, it was only necessary to read the temperature from each curve at a given value of P_R. From this temperature, the zero pressure enthalpy can be calculated, and, since the enthalpy of each curve is known, the quantity $(H^o-H_P)_T$ can be determined. Since the curves for CO_2 and N_2 covered a range of temperature from T_R = 0.80 to 2.5 or 3.0, it was possible to plot $(H^o-H_P)_T$ vs. T with values of P_R as parameters. These graphs were made large enough so that no appreciable error would result from cross-plotting, because values of $(H^o-H_P)_T$ vs. P_R with parameters of T_R were wanted. Values of $(H^o-H_P)_T$, therefore, were read at reduced temperatures of 0.80 to 1.20. The quantity $(H^o-H_P)_T/T_c$ was calculated, and the correlation made on the basis of these quantities.

The reduced temperature was read up to 1.20, because we wished to compare our work with that of York and Weber (49) which covered the T_R range 1.00 to 1.80.

Illustration of the Method.--We may illustrate the method of calculation of the isothermal enthalpy difference, $(H^o-H_p)_T$, by an example taken from the work on CO_2.

The following primary data are required:

(a) P-T data for isenthalps;

(b) Second virial coefficient data over the temperature range in question;

(c) C_p^o data over the temperature range in question.

First, the C_p^o data are fitted to an equation, covering the required temperature range, by the method of selected points. For CO_2 the equation, which shows an average deviation of 0.11% from observed values between 180 and 600°K (table 24) is found to be:

$$C_p^o = 204.662 + 0.645558T - 3.507088 \times 10^{-4}T^2 \quad \frac{cc\text{-}atm}{g\text{-}mole\text{-}^oK} \qquad (17)$$

This equation, when integrated and multiplied by a suitable conversion factor gives

$$H^o = 4.95615T + 7.816513 \times 10^{-3}T^2 - 2.830957 \times 10^{-6}T^3 \quad \frac{cal}{g\text{-}mole\text{-}^oK} \qquad (21)$$

Second virial coefficient data are then plotted against T, and a smooth curve is drawn through the points (fig. 1). From the curve, values of B are read at 5° intervals. A difference table is prepared, and $\frac{dB}{dT}$ is calculated from Newton's formula:

$$\frac{dB}{dT} = \frac{1}{h}\left[\Delta_1 B_o + (2p-1)\,\Delta_2\frac{B_o}{2} + (3p^2 - 6p + 2)\,\Delta_3\frac{B_o}{6} + (4p^3 - 18p^2 + 2p - 6)\cdot\frac{\Delta_4 B_o}{24} + (5p^4 - 40p^3 + 105p^2 - 100p + 24)\,\Delta_5\frac{B_o}{120}\right] \qquad (26)$$

where $p = (T-T_o)/h$, the lowest temperature in the difference table,

divided by h, the interval of T in the table, and where $\Delta_1 B_o$, $\Delta_2 B_o$, etc., are differences taken from the difference table.

Values from the difference table are substituted in this formula, and $\frac{dB}{dT}$ is calculated at T_f. For CO_2 isenthalp II-5, for example, T_f is 220.52°K, and the substitution of this value in Newton's formula, together with the corresponding values of ΔB_o, gives a value of 3.40 $\frac{cc}{°K}$ for $\frac{dB}{dT}$. C_p^o at 220.52°K is calculated to be 330.1 $\frac{cc\text{-}atm}{g\text{-}mole\text{-}°K}$, from equation (17). The value of B is gotten from the table by means of Newton's interpolating formula. This was done on this isenthalp, and all isenthalps with final temperatures below 220.52°K, because the slope of B vs. T curve is too large in this region for values to be determined graphically with sufficient accuracy. For higher temperatures, values of B were determined graphically. Then μ^o is calculated for equation (10). Here μ^o is found to be 3.01°K/atm.

The lowest pressure reported for isenthalp II-5 was 1.9 atmospheres. $(H^o-H_P)_T$ now can be calculated from equation (11):

$$(H^o-H_P)_{T_f} = \mu^o C_p^o P_f = T_f\left(\frac{dB}{dT}\right) - B\,P_f \qquad (11)$$

$$(H^o-H_P)_{T_f} = (992)\ (1.9) = 1884\ \frac{cc\text{-}atm}{g\text{-}mole} = 45.63\ \frac{cal}{g\text{-}mole}$$

Since $H^o = \int_o^T C_p^o dT = \left[\ 4.95615T + 7.816513 \times 10^{-3}T^2 - 0.830957 \times 10^{-6}T^3\right]_0^T$ (21)

when T = 220.52°K, H^o = 1442.7 $\frac{cal}{g\text{-}mole}$.

$$H^o-(H^o-H_P)_{T_f} = H = 1442.7 - 45.6 = 1397.1\ \frac{cal}{g\text{-}mole}$$

From the graph of this isenthalp, the temperature is read at P_R = 0.10, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00, and 2.50. At P_R = 0.10 and P_R = 0.25, the isenthalp is seen to be in the liquid region,

so no enthalpy difference calculation is possible. For all other points, the values of H° at the given temperatures are calculated from equation (21). Since H is the same all along the curve, the quantity $(H^{\circ}-H_P)_T$ is obtained for these values of P_R.

The enthalpy is determined for the other Joule-Thomson curves in the same way. Then temperatures are read at the above values of P_R for each Joule-Thomson curve. H° can be calculated for each of these points, and $(H^{\circ}-H_P)_T$ determined. Since the Joule-Thomson data cover a range of temperature, $(H^{\circ}-H_P)_T$ can now be plotted against T with P_R as parameter. From these graphs, $(H^{\circ}-H_P)_T$ can be read as a function of P_R with T_R as parameter. The method for correlating these data for the three substances considered will be discussed below.

Of the seven Joule-Thomson curves for CO_2, and the four for N_2, which fell below the critical temperature, only two of the CO_2 curves, and one of the N_2 curves, fall entirely above the vapor pressure curve. Actually, it was Roebuck's intention to determine the vapor pressure curve for CO_2, and he gives data for such a curve, derived from his Joule-Thomson measurements. Some of his Joule-Thomson curves are tangent to the vapor pressure curve at some points, and some of them pass into, then out of, the liquid region. Where the Joule-Thomson curve falls in the liquid region, equation (11) does not apply. Some points, therefore, are missing in our data, where the Joule-Thomson curve passes into the two-phase region. At $P_R = 0.50$, three of the four curves for N_2 are either in the saturated vapor region, or in the two-phase region.

Estimation of Error.--The chief source of error in the calculations of enthalpy differences lies in plotting and reading the P-T data. Roebuck

estimates his error in pressure measurement to be 0.15 atmosphere (11). The error in reading our P-T graph may be as large as 0.5 atmosphere, leading to an error in the enthalpy calculations of about 1.5%. Roebuck usually reported temperatures at intervals of 20-25 atmospheres, which makes the slope of the isenthalp uncertain at some points, and makes it more difficult to obtain accurate temperatures.

Another source of error in the calculations lies in the values chosen for the second virial coefficient. The identification of the enthalpy differences depends both on the value of B, and the value of the derivative, $\frac{dB}{dT}$. The quantity $T(\frac{dB}{dT})$ is usually several times larger than B. It is important, therefore, to estimate the accuracy of both B and $\frac{dB}{dT}$. The accuracy of B may be estimated from the manner in which the data scatter. There is no accurate means of determining the error in $\frac{dB}{dT}$. The slope may be in appreciable error, even if the error in B is small. The assumption was made that the error in $\frac{dB}{dT}$ is equal to the estimated error in B.

The derivative $\frac{dB}{dT}$ at a given point was taken in two different ways (by graphical measurement, and by the method of Newton), and variations in the result were observed. The percentage variation in the values for B at a given temperature, where more than one value was available, were noted. It appeared from these observations that five percent is sufficient allowance for error in B or $\frac{dB}{dT}$. Analysis of the isenthalps for CO_2 and N_2 showed that an error of five percent in B and $\frac{dB}{dT}$ results in an average error of about 0.65% in $(H^o-H_p)_T$ for CO_2, and an error of about 0.93% in $(H^o-H_p)_T$ for N_2. This analysis is made for N_2 and CO_2 in table 37. The calculation may be illustrated for N_2 isenthalp 1, as follows:

$T_f = 99.70^{\circ}K$; B at $T_f = -167 \frac{cc}{g\text{-mole}}$; $\frac{dB}{dT}$ at $T_f = 4.16 \frac{cc}{^{\circ}K}$ (table 33)

$P_f = 1.45$ atmospheres (table 34)

$167 \times 0.05 = 8.4 \frac{cc}{g\text{-mole}}$

$4.16 \times 0.05 = 0.208 \frac{cc}{^{\circ}K}$

$0.208 \times 99.70 = 20.8 \frac{cc}{g\text{-mole}}$

$20.8 + 8.4 = 29.2 \frac{cc}{g\text{-mole}}$

$29.2 \times 1.45 = 42.3 \frac{cc\text{-atm}}{g\text{-mole}}$, the estimated error $= 1.02 \frac{cal}{g\text{-mole}}$

At $P_R = 0.10$, $T = 103.86^{\circ}K$, $(H^{\circ}-H_P)_T = 49.4 \frac{cal}{g\text{-mole}}$ (table 35).

Percent error due to 5% error in B and $\frac{dB}{dT} = 1.02 \times \frac{100}{49.4} = 2.1\%$.

The percent error at $P_R = 0.25$, 0.50, 0.75, 1.00, and 1.25 for this isenthalp is found the same way. The average error for this isenthalp is found to be 1.0%.

In table 22, values of μ for CO_2, taken from the table of Roebuck, et al., (11) are compared with values calculated by de Groot and Michels from compressibility data at one atmosphere (8). The agreement is quite good. In table 33, values of μ° which we calculated for N_2 are compared with values calculated independently by Lunbeck, et al., (9). The agreement is excellent. Deming and Deming (10) also have compared values for the Joule-Thomson coefficient for N_2, which they calculated from compressibility data, with the experimental values of Roebuck and Osterberg (5), and they found an average difference of 2.4%, when high percentage divergences (where μ is small) were excluded. Deming states that the numerical divergences between the μ's, where μ is small, averaged only 0.007 $^{\circ}C$/atmosphere (10).

The Joule-Thomson data of Roebuck and co-workers on CO_2 and N_2, therefore, is in agreement with values calculated from compressibility data, while our values for μ° for N_2 are also in agreement with values calculated independently. These facts make it apparent that the Joule-Thomson data on which our calculations are based are quite accurate.

The enthalpy differences for steam are assumed to be quite accurate. Keyes states that the calculations from various sources were in agreement to about one part in a thousand (12).

These estimates of error are based on the assumption that C_p° data, and the equation for H°, are not in error. We have calculated enthalpy differences, $(H^\circ-H_P)_T$, and the equation for H° is used in the identification of both H and H°. An error in C_p°, therefore, introduces compensating errors. Calculation showed that an error of 0.10% in C_p° for CO_2 led to no detectable error in the quantity $(H^\circ-H_P)_T$ for isenthalp I-8 at temperatures of 300-400°K.

The average error in the enthalpy difference calculations is believed to be about 2.2% for CO_2, and about 2.4% for N_2.

In the calculation of the individual enthalpy differences for each substance, the percentage error is greater at low values of P_R, because the quantity $(H^\circ-H_P)_T$ is smaller, while the numerical error decreases less rapidly than the enthalpy difference. In table 37, the percentage error, due to errors in the second virial coefficient and its derivative, is shown to vary from 0.2% to 2.1%. The error due to inaccuracy in reading the isenthalpic plot of P vs. T is independent of P, and therefore the percentage error from this source increases with decreasing pressure. At 100°K, an error of 1.0° in reading the temperature,

resulting from an error of 0.5 atmosphere in reading the pressure, results in an error of 7 calories in $(H^{\circ}-H_P)_T$ for N_2. An error of this magnitude is quite large when $P_R = 0.10$, where the enthalpy difference is 50 $\frac{cal}{g\text{-mole}}$.

For CO_2, an error of 1.0° in reading a temperature, resulting from an error of 0.5 atmosphere in reading a pressure on an isenthalp, results in an error of 5 $\frac{cal}{g\text{-mole}}$ in $(H^{\circ}-H_P)_T$ at $230^{\circ}K$. At this temperature, and at a reduced pressure of 0.10, $(H^{\circ}-H_P)_T$ is 160 calories per gram mole.

The maximum error in the quantity $(H^{\circ}-H_P)_T$ for nitrogen, therefore, is about 15%, while the maximum error for CO_2 is about 4.5%. These large errors apply only at $P_R = 0.10$, and they decrease rapidly as the temperature and pressure rise. For example, when $P_R = 0.25$, at $115^{\circ}K$, the error in $(H^{\circ}-H_P)_T$ for nitrogen due to an error of 0.5 atm in reading P, would be less than 7%.

Comparison with the Work of Others.--Our isothermal enthalpy differences for CO_2 differ from those of Michels (50) over the range covered by both sets of data, by an average of 4.5% (table 29). Michels gives no data below the critical temperature. The enthalpy differences between the isenthalps differ from the differences obtained by interpolation from the tables of Sweigert, et al., (51) by - 1.5% (table 29). The enthalpy differences between isenthalps for N_2 differ from those obtained by interpolation from the tables of Bloomer and Rao (31) by about -0.7%. Our enthalpy differences for N_2 can be compared with the values of Lunbeck, et al., (9) only at 50 atmospheres, at which pressure our values differ from those of Lunbeck, et al., by an average of -3.0% (table 36).

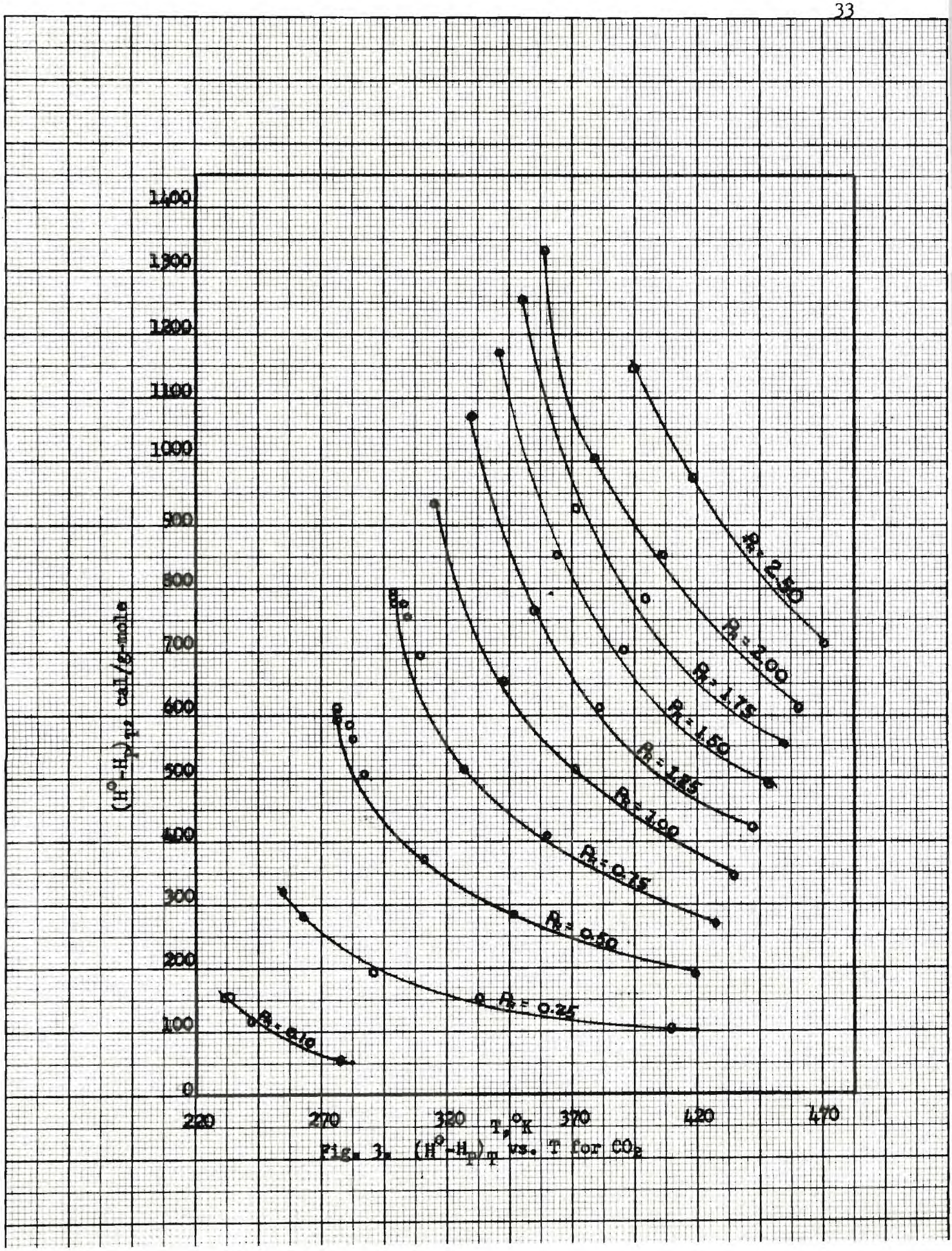

Fig. 3. $(H^\circ - H_{298})_T$ vs. T for CO_2

Table 10. Enthalpy Differences, $(H^{\circ}-H_P)_T$, For CO_2

Read from Graph of $(H^{\circ}-H_P)_T$ vs. T (Fig. 2)

T_R	T, °K	P_R	$(H^{\circ}-H_P)_T$, cal/g-mole	$\frac{(H^{\circ}-H_P)_T}{T_c}$
0.80	243.35	0.10	119	0.394
0.85	258.56	0.10	89	0.292
0.90	273.77	0.10	65	0.213
0.85	258.56	0.25	302	0.993
0.90	273.77	0.25	247	0.812
0.95	288.98	0.25	210	0.690
0.95	288.98	0.50	496	1.629
1.00	304.19	0.25	185	0.608
1.00	304.19	0.50	398	1.305
1.00	304.19	0.75	724	2.370
1.10	334.61	0.25	149	0.490
1.10	334.61	0.50	310	1.018
1.10	334.61	0.75	487	1.600
1.10	334.61	1.00	702	2.305
1.10	334.61	1.25	994	3.258
1.20	365.03	0.25	124	0.407
1.20	365.03	0.50	255	0.839
1.20	365.03	0.75	396	1.300
1.20	365.03	1.00	540	1.775
1.20	365.03	1.25	690	2.265

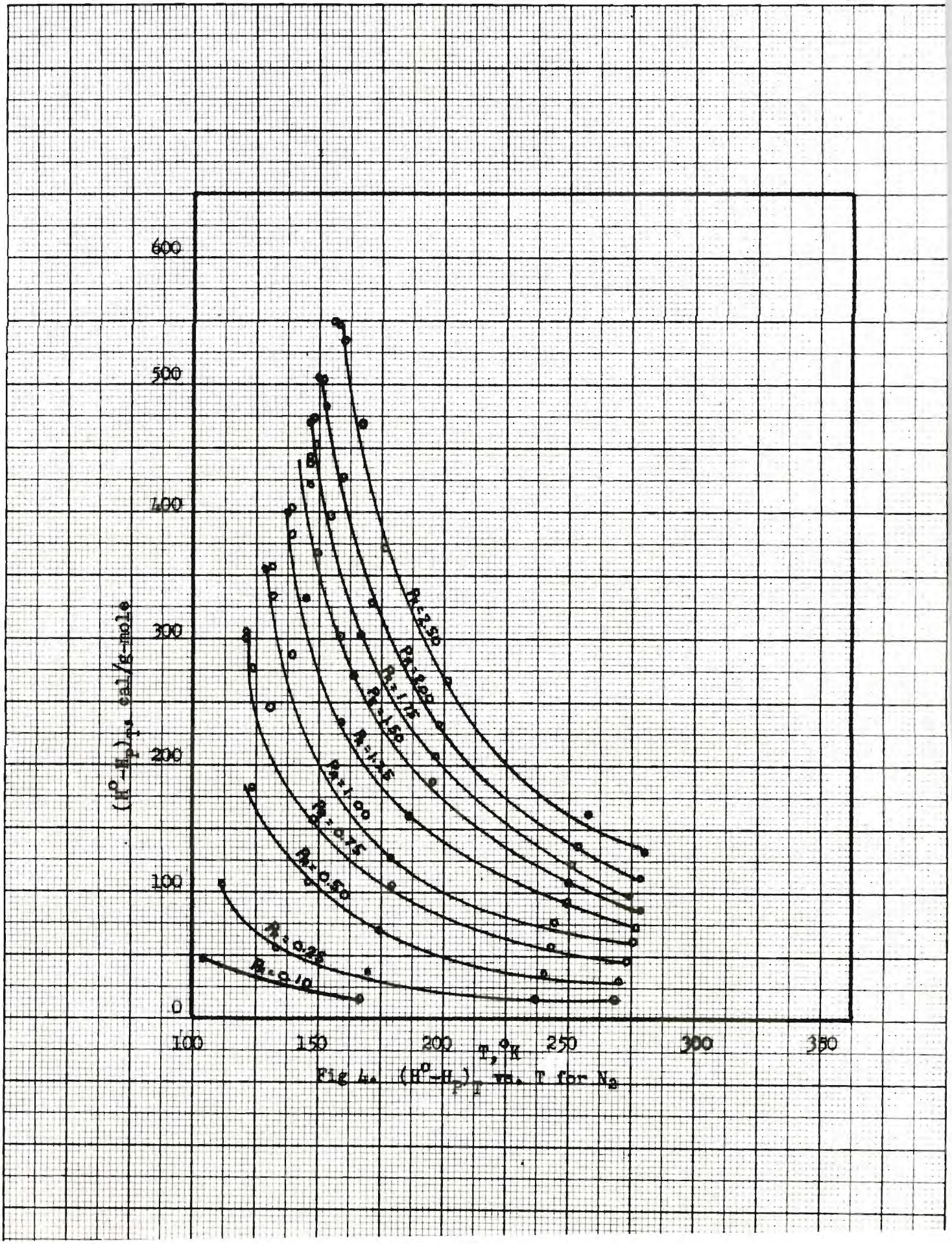

Fig 4. $(H^o-H_p)_T$ vs. T for N_2

Table 11. Enthalpy Differences, $(H^{\circ}-H_P)_T$, For N_2

Read from Graph of $(H^{\circ}-H_P)_T$ vs. T (Fig. 4)

T_R	T, °K	P_R	$(H^{\circ}-H_P)_T$, $\frac{cal}{g\text{-mole}}$	$\frac{(H^{\circ}-H_P)_T}{T_c}$
0.85	107.52	0.10	45	0.358
0.90	113.63	0.10	40	0.316
0.95	119.95	0.10	36	0.284
0.90	113.63	0.25	102	0.806
0.95	119.95	0.25	82	0.648
0.95	119.95	0.596	220	1.742
1.00	126.26	0.25	69	0.545
1.00	126.26	0.50	162	1.282
1.00	126.26	0.596	181	1.426
1.00	126.26	0.75	263	2.082
1.10	138.89	0.25	53	0.418
1.10	138.89	0.50	118	0.932
1.10	138.89	0.596	139	1.096
1.10	138.89	0.75	192	1.513
1.10	138.89	1.00	272	2.148
1.10	138.89	1.25	366	2.885
1.20	151.51	0.25	44	0.347
1.20	151.51	0.50	96	0.758
1.20	151.51	0.596	113	0.893
1.20	151.51	0.75	151	1.191
1.20	151.51	1.00	209	1.655
1.20	151.51	1.25	270	2.125

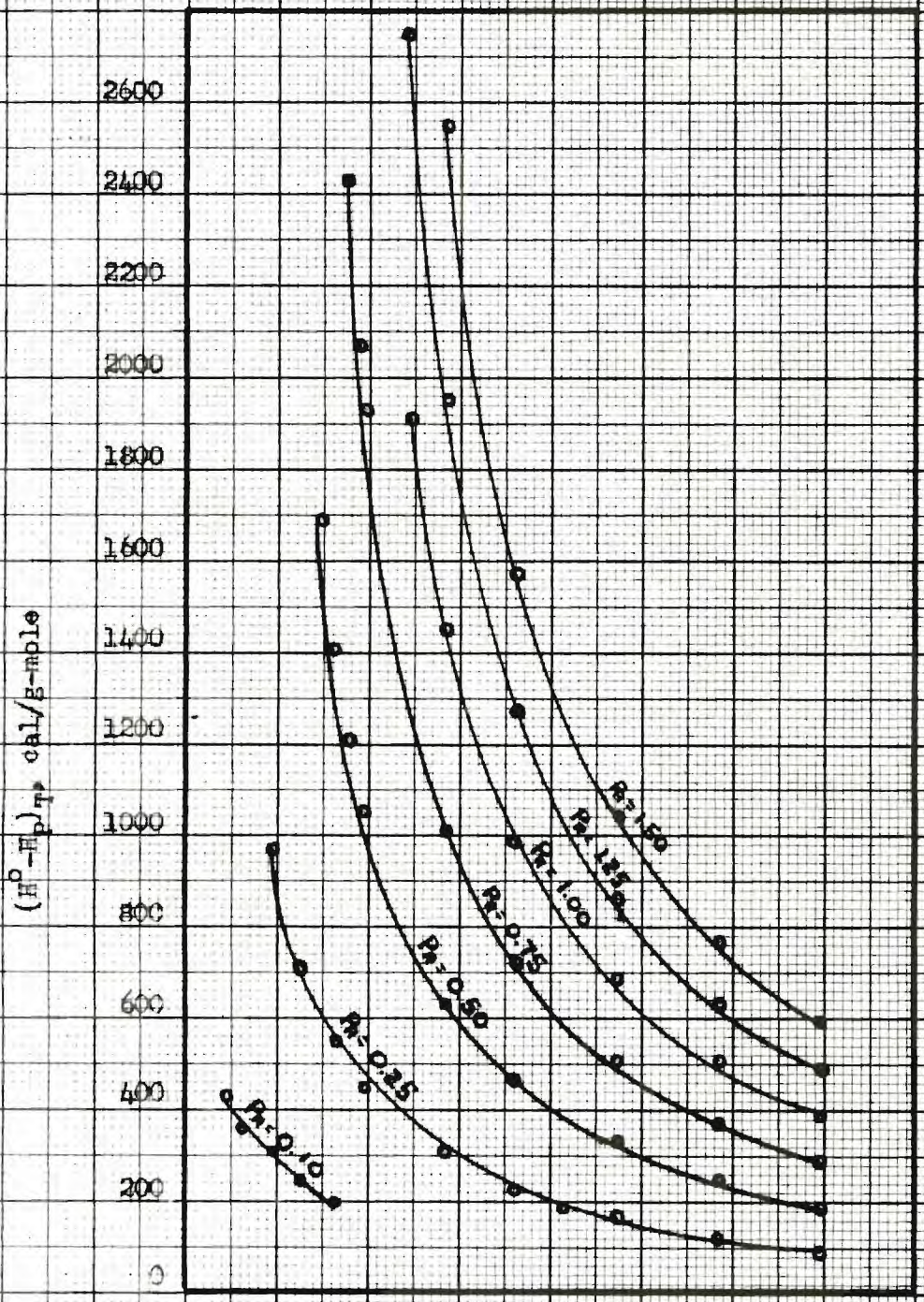

Fig. 5. $(H^o-H_p)_T$ vs. T for H_2O

Table 12. Enthalpy Differences, $(H^{\circ}-H_P)_T$, For H_2O

Read from Graph of $(H^{\circ}-H_P)_T$ vs. T (Fig. 5)

T_R	T, °K	P_R	$(H^{\circ}-H_P)_T$, $\frac{cal}{g\text{-mole}}$	$\frac{(H^{\circ}-H_P)_T}{T_c}$
0.80	517.82	0.10	368	0.569
0.85	550.18	0.10	300	0.464
0.85	550.18	0.25	912	1.412
0.90	582.54	0.10	240	0.371
0.90	582.54	0.25	690	1.065
0.95	614.91	0.10	194	0.300
0.95	614.91	0.25	545	0.843
0.95	614.91	0.50	1350	2.085
1.00	647.27	0.25	452	0.711
1.00	647.27	0.50	1038	1.604
1.00	647.27	0.75	1884	2.91
1.00	647.27	1.00	4820	7.46
1.10	712.00	0.25	327	0.506
1.10	712.00	0.50	705	1.089
1.10	712.00	0.75	1154	1.785
1.10	712.00	1.00	1660	2.57
1.10	712.00	1.25	2270	3.51
1.20	776.72	0.25	255	0.394
1.20	776.72	0.50	527	0.815
1.20	776.72	0.75	826	1.277
1.20	776.72	1.00	1153	1.785
1.20	776.72	1.25	1510	2.335

CHAPTER V

CORRELATION OF $\frac{(H^{\circ}-H_P)_T}{T_c}$ WITH REDUCED TEMPERATURE AND REDUCED PRESSURE

Some Existing Correlations.--The "law of corresponding states" is not a law, but a statement of the approximation that the thermodynamic properties of a gas are roughly proportional to the reduced temperature and the reduced pressure of the gas. This approximation has been very useful, and the compressibility factor, activity coefficient, and isothermal enthalpy difference have been represented graphically as functions of T_R and P_R.

A graph of $\frac{(H^*-H_P)_T}{T}$ vs. P_R, with T_R as parameter, has been given by Watson and Smith (3). In this graph, $(H^*-H_P)_T$ is the difference between the enthalpy of a substance at atmospheric pressure, and that at an elevated pressure, along an isotherm. The values were obtained from the relation

$$\frac{(H^*-H_P)_T}{T} = R \left(\frac{\partial \ln \lambda}{\partial \ln T_R} \right)_{P_R} \qquad (27)$$

by graphical differentiation of a graph of activity coefficient vs. T_R with P_R as parameter.

Watson and Nelson (2) obtained the enthalpy difference from the expression

$$\frac{(H^{\circ}-H_P)_T}{T_c} = RT_R^2 \int_0^{P_R} \left(\frac{\partial c}{\partial T_R} \right)_{P_R} d \ln P_R \qquad (28)$$

The derivative $\left(\frac{\partial c}{\partial T_R}\right)_{P_R}$ was obtained by graphical differentiation of a compressibility chart. This correlation was corrected by Hougen and Watson (52) to represent an average of the calculations made by Edmister (53) and by York and Weber (49).

York and Weber expressed the enthalpy difference, $\frac{(H^o-H_P)_T}{T_c}$ as a function of the enthalpy difference for a reference substance (C_3H_8) and of P_R and T_R. Thus

$$\left(\frac{H^o-H_P}{T_c}\right)_i = \left(\frac{H^o-H_P}{T_c}\right)_{C_3H_8} \left(\frac{T_{c_i}}{T_{c_{C_3H_8}}}\right)^n \qquad (29)$$

where the subscript i refers to any substance, while the subscript C_3H_8 refers to propane. The value of n was assumed to be independent of pressure, which means that the curves on the graph of $\frac{(H^o-H_P)_T}{T_c}$ could be made to coincide by dividing by a function of T_R.

York and Weber calculated the value of the exponent n from known enthalpy differences, and plotted the values of n so obtained against T_R. They then calculated a function ϕ for these substances, where

$$\phi = f(T_R) = \left(\frac{T_{c_i}}{T_{c_{C_3H_8}}}\right)^n \qquad (30)$$

and plotted $\frac{H^o-H}{\phi T_c}$ for each substance against P_R, with T_R as parameter. All of these points should fall on a single curve for each value of the parameter because, if the correlation were perfect, each quantity of $(H^o-H_P)_T$ would be equal to the value for C_3H_8 at corresponding values of T_R and P_R.

This graph is reproduced in York and Weber's paper, and most of the points fall on a single curve at each value of T_R. As an independent check of their correlation, York and Weber compared values obtained from it for CO_2 with values given by Michels (50), and values obtained for C_6H_6 with values given by Lindsay and Brown (13). Good agreement was obtained in the case of CO_2, and fair agreement in the case of C_6H_6.

The correlation of York and Weber covered the range between T_R = 1.00 and 1.80, and P_R = 0 and 8.0. They say that it is reliable for hydrocarbons with critical temperatures between 300 and 600°K (49).

Description of the Correlation Method Used in This Thesis.--In the graph of York and Weber, which gives n as a function of T_R, the slope appears to be increasing as T_R decreases, showing that the correction to the enthalpy difference is becoming greater as T_R decreases. The slope of the curve appears to be quite large at T_R = 1.0. This suggests that the correction might be greater below T_R = 1.0.

It was our purpose to use the enthalpy differences calculated by us from Joule-Thomson data to examine the possible applicability of a correlation, in the range below T_c, similar to that obtained by York and Weber (49) in the range above T_c. One can see by reference to table 14, that values for $(H^o-H_P)_{T_c}$ obtained from the correlation of Hougen and Watson (52) show large deviations from observed values, when T_R = 1.00, indicating that some correction must be applied to the Hougen and Watson correlation in the range below T_c.

The observed enthalpy differences are plotted against temperature for CO_2, N_2, and H_2O in figures 3, 4, and 5. Points were read from these curves at reduced temperatures of 0.80, 0.85, 0.90, 0.95, 1.00, 1.10, and

1.20, at various reduced pressures. Using water as a reference substance, the value of the exponent n in the relation

$$\frac{H^{\circ}-H_P}{(T_c)_i} = \left(\frac{(H^{\circ}-H_P)_T}{T_c}\right)_{H_2O} \left(\frac{T_{c_i}}{T_{c_{H_2O}}}\right)^n \qquad (31)$$

was calculated for these values of reduced temperature and pressure. Use of equation (31) may be illustrated by a specific example for CO_2. At $P_R = 1.0$, $P_R = 0.25$, from table 10, and table 12, $\frac{(H^{\circ}-H_P)_T}{T_c}$ for water is seen to be 0.711, and $\frac{(H^{\circ}-H_P)_T}{T_c}$ for CO_2 is 0.608. From equation (31),

$$\left(\frac{T_cCO_2}{T_cH_2O}\right)^n = \frac{\left(\frac{(H^{\circ}-H_P)_T}{T_c}\right)_{CO_2}}{\left(\frac{(H^{\circ}-H_P)_T}{T_c}\right)_{H_2O}} = 0.853$$

$$\left(\frac{T_{c_{CO_2}}}{T_{c_{H_2O}}}\right) = \frac{304.19}{647.27} = 0.471$$

$$n \log 0.471 = 0.853$$

$$n = 0.212$$

Values of n obtained in this way were plotted against T and a smooth curve drawn (fig. 6). The values for n used in this thesis were taken from such a curve, and are tabulated in table 41. If n were independent of pressure, the points would fall on a smooth curve. Such a plot has been prepared by York and Weber (49), covering a temperature range between $T_R = 1.0$ and $T_R = 1.80$, and most of their points do fall on a smooth curve. However, in the temperature range between $T_R = 0.80$ and 1.00, we found that the points often fall far off the curve, particularly at lower reduced temperatures.

Values of n were read at reduced temperatures of 0.80, 0.85, 0.90, 0.95, 1.00, 1.10, and 1.20, and values of ϕ were calculated from the relation

$$\phi = \left(\frac{(T_c)_{CO_2}}{(T_c)_{H_2O}}\right)^n \tag{32}$$

For example, when $T_R = 1.00$, $n = 0.16$ (fig. 6) and

$$\phi = (0.041)^{0.16} = 0.886$$

From table 10, at $T_R = 1.00$, $P_R = 0.25$, $\frac{(H^\circ - H_P)_T}{T_c}$ for $CO_2 = 0.608$

$$\frac{(H^\circ - H_P)_T}{\phi T_c} = \frac{0.608}{0.886} = 0.688$$

Values of $\frac{(H^\circ - H_P)_T}{\phi T_c}$ for CO_2 and N_2, obtained in this way, are plotted against P_R, with T_R as parameter, in figures 7 and 8. For water, of course, $\phi = 1$, and values of $\frac{(H^\circ - H_P)_T}{T_c}$ are plotted. There is some scattering when $T_R = 1.00$, particularly at $P_R = 0.10$, but, in general, the points fall along a fairly smooth curve.

In order to obtain the enthalpy difference, $(H^\circ - H_P)_T$, for any substance from figure 7 or figure 8, the value of the ordinate is read at the appropriate reduced temperature and pressure. The value of n is taken at the appropriate reduced temperature from figure 6, and ϕ is calculated. Then $(H^\circ - H_P)_T$ can be determined as follows:

$$(H^\circ - H_P)_T = \frac{(H^\circ - H_P)_T}{\phi T_c} \cdot \phi \cdot T_c \tag{33}$$

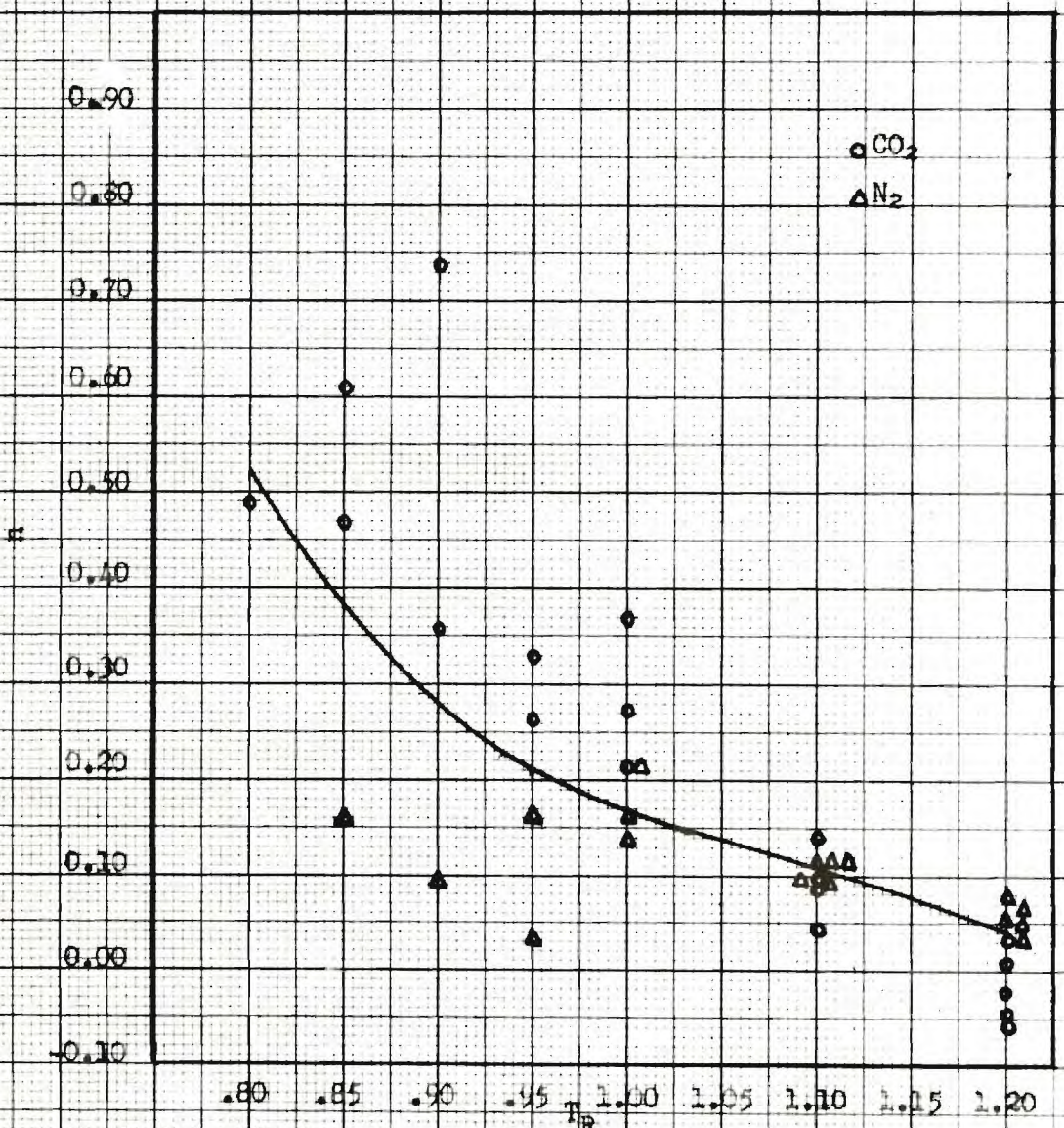

Fig. 6. Exponent of the Correction Factor vs. T_R, for CO_2 and N_2

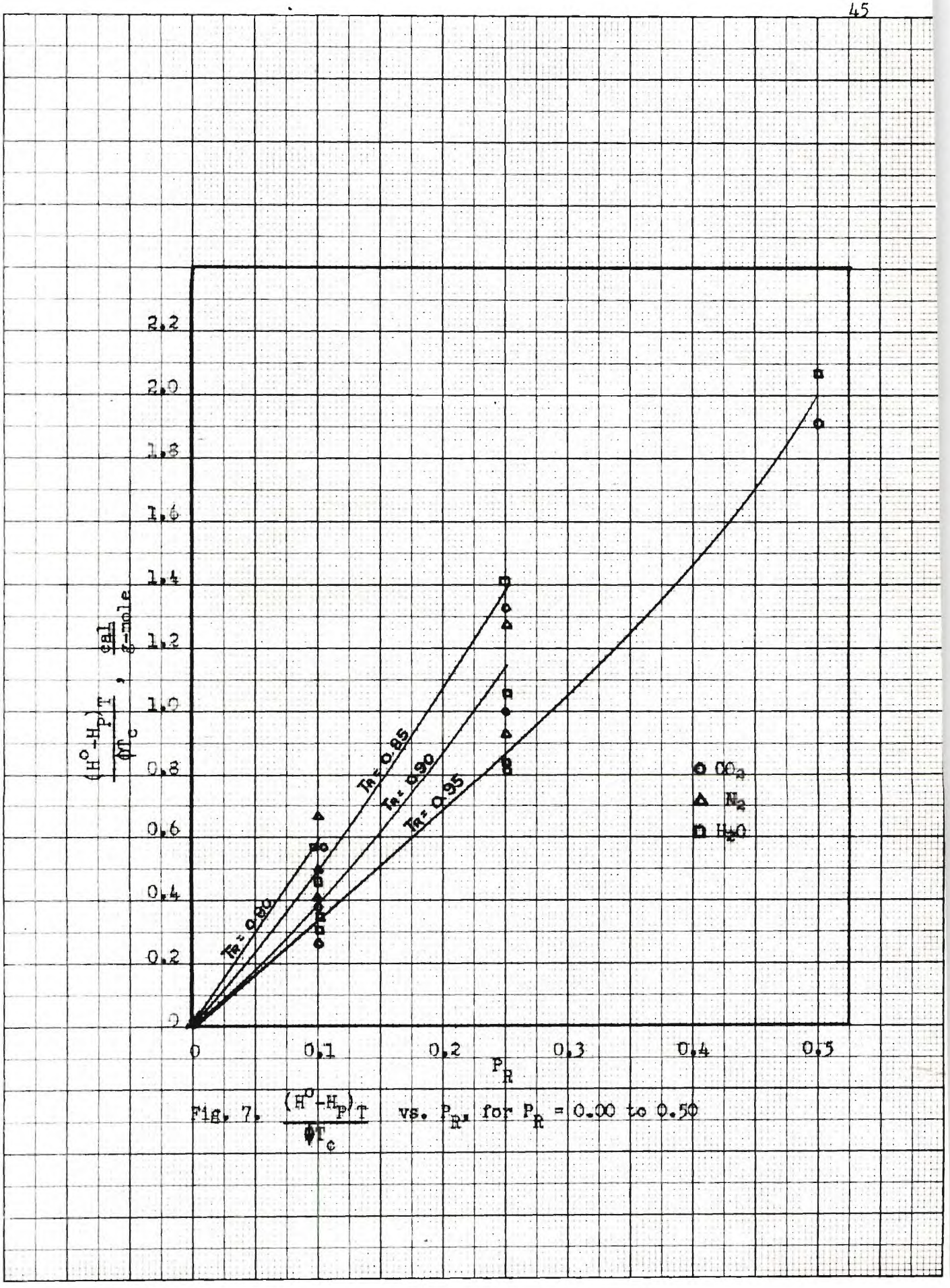

Fig. 7. $\frac{(H^o-H_p)T}{\phi T_c}$ vs. P_R, for P_R = 0.00 to 0.50

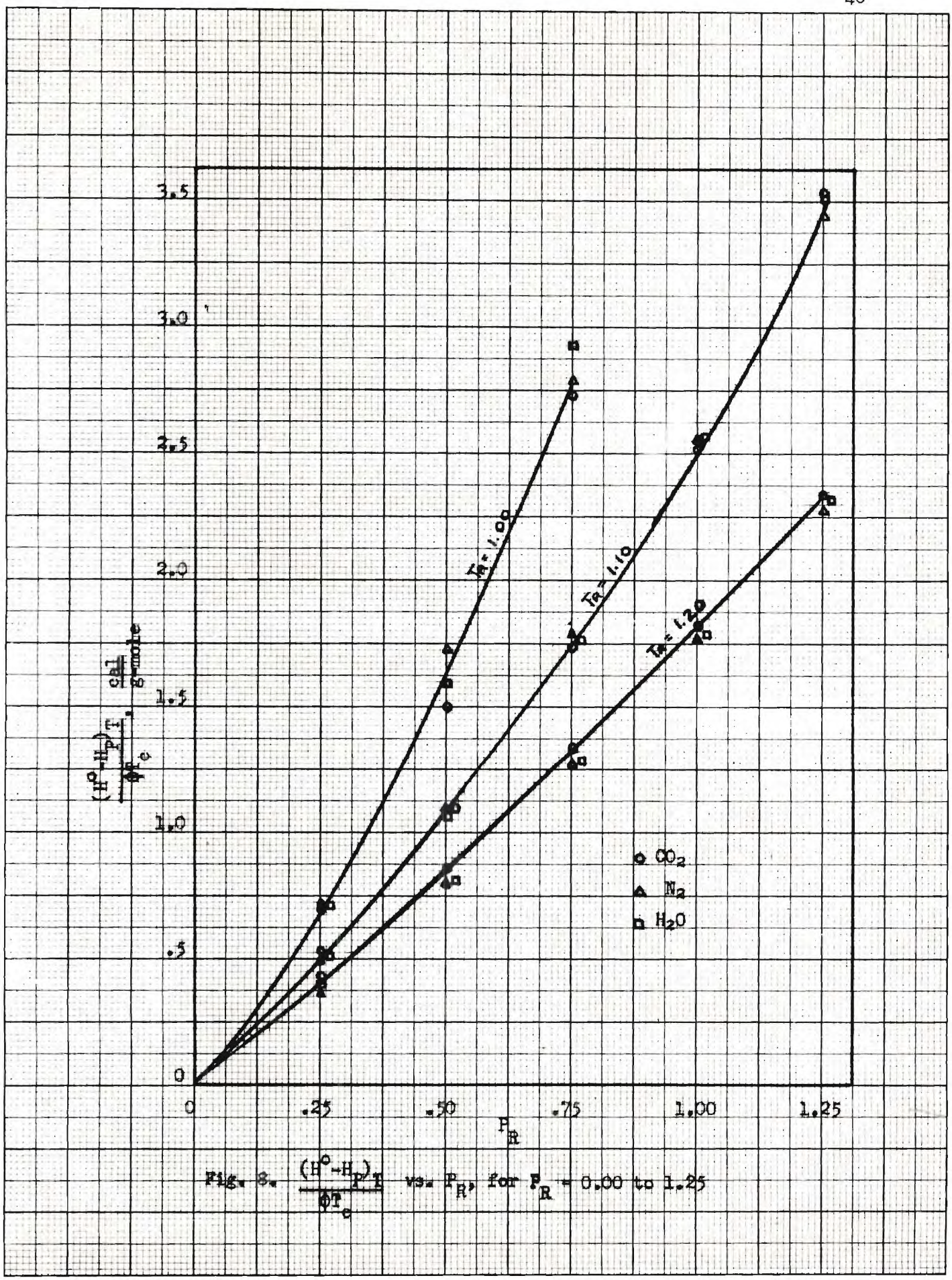

Fig. 8. $\frac{(H^o-H_P)T}{\phi T_c}$ vs. P_R, for P_R = 0.00 to 1.25

Table 13 shows that the difference between the observed value and the value obtained from our correlation for the enthalpy difference for CO_2 at $T_R = 1.00$, $P_R = 0.25$ is 1.7%. We note that the observed and correlated values of the enthalpy difference are in close agreement here, although the calculated and correlated values of n differ by about 32%.

Table 13 was prepared to show how well the correlation would reproduce the observed values of $\frac{(H^o-H_P)_T}{T_c}$. It is seen that these values of $\frac{(H^o-H_P)_T}{T_c}$ are reproduced quite well in the range where $T_R = 1.00$. Appreciable deviations occur chiefly at $P_R = 0.10$.

Comparison With the Work of Others.--Comparison of tables 14, 15, and 16, with table 13, shows that our correlation gives better values for $\frac{(H^o-H_P)_T}{T_c}$ for the three substances for which it was derived, than the correlation of Watson and Smith, or of Hougen and Watson*, with or without the correction of York and Weber. In some cases, our correlation is much better. In table 17, the deviations in percent of correlation values of $\frac{(H^o-H_P)_T}{T_c}$ from observed values for H_2O, CO_2, and N_2 have been averaged for each of the correlations considered. Our correlation shows a smaller average percentage deviation for these three substances than the correlation of Watson and Smith, or the correlation of Hougen and Watson, with or without the correction of York and Weber.

Values of $\frac{(H^o-H_P)_T}{T_c}$ for benzene and n-pentane, which we calculated

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*Values of $(H^o-H_P)_T$ were taken from the charts of Hougen and Watson (52) as they appear in their work without a correction factor. Comparisons are also made with values of $(H^o-H_P)_T$ obtained by applying the correction factor of York and Weber (49) to values of $(H^o-H_P)_T$ taken from the charts of Hougen and Watson.

from the data of Lindsay and Brown, are used to check our correlation independently. In tables 20 and 21 these calculated values are compared with values obtained from this correlation, from the correlation of Hougen and Watson, and from the correlation of Watson and Smith. For benzene, the average deviation observed for our correlation is 11.8%, while for the Hougen and Watson correlation it is 9.9%. For n-pentane, the average deviation for this correlation is 5.3%, while for the Hougen and Watson correlation it is 6.7%. Thus, the average deviation for both substances for these two correlations is almost identical. The value of the quantity $\frac{(H^{\circ}-H_P)_T}{T_c}$, obtained from the correlation of Watson and Smith deviated from the observed value by 24.3%, in the case of benzene, and by 19.0%, in the case of n-pentane. Our correlation, therefore, gives much better results for these two substances than that of Watson and Smith.

Table 13. Comparison of Observed Values for $(H^{o}-H_{p})_{T}$

With Values Obtained from This Correlation

T_R	P_R	Observed			This Correlation			Percent Deviation = (Observed-Correlation) / Observed x .01		
		H_2O	CO_2	N_2	H_2O	CO_2	N_2	H_2O	CO_2	N_2
0.80	0.10	0.57	0.39	-	0.58	0.39	0.25	+1.8	0.0	0.0
0.85	0.10	0.46	0.29	0.36	0.49	0.34	0.26	-6.5	-17.3	+27.9
0.85	0.25	1.41	0.99	-	1.39	1.04	0.74	+1.4	-4.8	-
0.90	0.10	0.37	0.21	0.32	0.38	0.31	0.23	+2.7	-47.0	+28.0
0.90	0.25	1.07	0.81	0.81	1.13	0.91	0.71	+5.6	-12.3	+12.4
0.95	0.10	0.30	-	0.28	0.32	0.27	0.23	-6.7	-	+17.6
0.95	0.25	0.84	0.69	0.65	0.85	0.72	0.60	-1.2	-4.3	+7.7
0.95	0.50	2.09	1.63	-	2.00	1.71	1.42	+4.3	-4.9	-
1.00	0.25	0.71	0.61	0.55	0.68	0.60	0.52	+4.2	+1.7	+7.3
1.00	0.50	1.60	1.31	1.28	1.60	1.42	1.23	0.0	-8.4	+7.1
1.00	0.75	2.91	2.37	2.07	2.78	2.46	2.08	+4.5	-3.8	-0.5
1.10	0.50	1.09	1.02	0.93	1.08	0.99	0.90	+0.9	+3.0	+3.2
1.10	0.75	1.80	1.60	1.51	1.76	1.62	1.47	+2.2	-1.2	-1.3
1.10	1.00	2.57	2.31	2.15	2.52	2.32	2.10	+1.9	-0.4	-2.3
1.10	1.25	3.51	3.26	2.89	3.50	3.22	2.88	+2.0	-1.2	+2.4
1.20	0.50	0.82	0.84	0.76	0.82	0.80	0.77	0.0	-4.8	-1.3
1.20	0.75	1.28	1.30	1.19	1.34	1.30	1.26	-4.7	0.0	-5.9
1.20	1.00	1.70	1.78	1.66	1.84	1.70	1.73	-2.8	-0.6	-4.2
1.20	1.25	2.34	2.27	2.13	2.32	2.24	2.17	+0.9	+1.3	-1.9

Table 14. Comparison of Observed Values of $\frac{(H^{\circ}-H_P)_T}{T_c}$

With Values Obtained from Correlation of Hougen and Watson

T_R	P_R	$(H^{\circ}-H_P)_T/T_c$ Observed H_2O	CO_2	N_2	$\frac{(H^{\circ}-H_P)_T}{T_c}$ Hougen, Watson	Percent Deviation = (Observed-Correlation) 100 / Observed H_2O	CO_2	N_2
0.80	0.10	0.57	0.39	-	0.52	8.8	33.3	-
0.85	0.10	0.46	0.29	0.36	0.43	6.5	48.3	19.4
0.85	0.25	1.41	0.99	-	1.25	11.3	19.3	-
0.90	0.10	0.37	0.21	0.32	0.35	5.4	66.6	9.4
0.90	0.25	1.07	0.81	0.81	0.96	10.3	18.5	18.6
0.95	0.10	0.30	-	0.28	0.28	6.7	-	0.0
0.95	0.25	0.84	0.69	0.65	0.78	7.1	13.1	20.0
0.95	0.50	2.09	1.63	-	1.9	9.1	16.6	-
1.00	0.25	0.71	0.61	0.55	0.62	12.7	1.6	12.7
1.00	0.50	1.60	1.31	1.28	1.40	12.5	6.9	9.4
1.00	0.75	2.91	2.37	2.08	2.50	14.1	5.5	20.8
1.10	0.50	1.09	1.02	0.93	1.05	3.7	2.9	12.9
1.10	0.75	1.80	1.60	1.51	1.7	5.6	6.3	12.6
1.10	1.00	2.57	2.31	2.15	2.5	2.7	8.2	16.2
1.10	1.25	3.51	3.26	2.89	3.6	2.5	9.7	24.6
1.20	0.50	0.82	0.84	0.76	0.90	9.8	7.2	18.4
1.20	0.75	1.28	1.30	1.19	1.42	10.9	9.2	19.7
1.20	1.00	1.79	1.78	1.66	1.90	5.6	6.8	14.5
1.20	1.25	2.34	2.27	2.13	2.50	6.8	10.1	17.4

Table 15. Comparison of Observed Values of $\frac{(H^{\circ}-H_P)_T}{T_c}$ With

Values Obtained from Correlation of Watson and Smith

T_R	P_R	$(H^{\circ}-H_P)_T/T_c$ Observed H_2O	CO_2	N_2	Watson and Smith	Percent Deviation = (Observed-Correlated) 100 / Observed H_2O	CO_2	N_2
0.80	0.10	0.57	0.39	-	0.32	44.0	17.9	-
0.85	0.10	0.46	0.29	0.36	0.30	34.8	3.5	16.7
0.85	0.25	1.41	0.99	-	0.99	33.6	0.0	-
0.90	0.10	0.37	0.21	0.32	0.27	27.0	28.6	15.7
0.90	0.25	1.07	0.81	0.81	0.90	15.8	11.1	11.1
0.95	0.10	0.30	-	0.28	0.38	26.6	-	35.6
0.95	0.25	0.84	0.69	0.65	0.71	15.5	2.9	0.0
0.95	0.50	2.09	1.63	-	1.62	22.5	1.6	-
1.00	0.25	0.71	0.61	0.55	0.60	15.5	1.6	9.1
1.00	0.50	1.60	1.31	1.28	1.4	12.5	6.9	9.4
1.00	0.75	2.91	2.37	2.08	2.7	7.2	13.9	30.4
1.10	0.50	1.09	1.02	0.93	1.1	0.9	7.8	18.3
1.10	0.75	1.80	1.60	1.51	1.8	0.0	12.5	19.2
1.10	1.00	2.57	2.31	2.15	2.5	5.6	8.2	16.3
1.10	1.25	3.51	3.26	2.89	3.3	6.0	1.2	14.2
1.20	0.50	0.82	0.84	0.76	.72	12.2	14.3	5.3
1.20	0.75	1.28	1.30	1.19	1.2	6.2	7.7	0.8
1.20	1.00	1.79	1.78	1.66	1.8	0.6	1.1	8.4
1.20	1.25	2.34	2.27	2.13	2.3	1.7	1.3	8.0

Table 16. Comparison of Observed Values for $\frac{(H^{o}-H_{P})_{T}}{T_{c}}$ With Values Obtained from Correlation of Hougen and Watson (52) After Applying the Correction of York and Weber (49)

T_R	P_R	$(H^{o}-H_{P})_{T}/T_{c}$ Observed H_2O	Observed CO_2	Observed N_2	Hougen-Watson-York H_2O	Hougen-Watson-York CO_2	Hougen-Watson-York N_2	Percent Deviation = (Observed-Correlation)/Observed x .01 H_2O	CO_2	N_2
1.00	0.25	0.71	0.61	0.55	0.77	0.58	0.41	8.4	4.9	25.4
1.00	0.50	1.60	1.31	1.28	1.73	1.30	0.93	8.1	0.8	27.4
1.00	0.75	2.91	2.37	2.08	3.09	2.32	1.66	6.2	2.1	19.8
1.10	0.50	1.09	1.02	0.93	1.21	0.97	0.80	11.0	4.9	14.0
1.10	0.75	1.80	1.60	1.51	1.96	1.62	1.30	8.9	1.2	13.9
1.10	1.00	2.57	2.31	2.15	2.88	2.38	1.91	12.0	3.0	11.1
1.10	1.25	3.51	3.26	2.89	4.15	3.44	2.74	18.2	5.1	5.2
1.20	0.50	0.82	0.84	0.76	1.02	0.87	0.72	24.4	3.6	5.3
1.20	0.75	1.28	1.30	1.19	1.59	1.37	1.14	24.2	5.4	4.2
1.20	1.00	1.79	1.78	1.66	2.13	1.83	1.53	18.9	2.8	7.8
1.20	1.25	2.34	2.27	2.13	2.80	2.40	2.02	19.7	5.7	5.2

Table 17. Average Deviations in Percent Between Observed Values for $(H^{o}-H_{P})_{T}/T_{c}$ for H_2O, CO_2, and N_2, and Values Obtained From our Correlation and Values Obtained from Other Correlations

	H_2O	CO_2	N_2
This Correlation	2.8	6.5	8.2
Hougen and Watson	8.0	16.1	15.4
Watson and Smith	15.2	7.8	13.7
at $T_R \geq 1.0$			
This Correlation	2.1	2.4	3.1
Hougen and Watson, corrected by York and Weber's Factor	14.6	3.6	12.7

Table 18. Values of $(H^{o}-H_{P})_{T}$ for Benzene, Obtained From Joule-Thomson Experiments of Lindsay and Brown (13)

Run	T, °K	P, Atm	T_R	P_R	H^{o}, $\frac{cal}{g\text{-mole}}$	H, $\frac{cal}{g\text{-mole}}$	$(H^{o}-H_{P})_{T}$
1	510.3	8.23	0.908	0.171	7707.2	7384.9	322.3
5	576.4	24.77	1.025	0.513	10060.5	9345.7	714.8
8	459.2	5.24	0.815	0.108	6054.1	5639.4	414.7
9	655.8	24.29	1.167	0.503	73169.4	12669.8	499.6
14	590.8	46.41	1.051	0.962	10602.8	9064.4	1538.4
34	513.2	7.62	0.913	0.158	7801.9	7468.2	333.7
60	662.5	45.73	1.179	0.950	13444.7	12404.2	1040.5

Table 19. Values of $(H^{o}-H_{P})_{T}$ For n-Pentane, Obtained From the Joule-Thomson Experiments of Pattee and Brown (14)

Test	T, °K	P, Atm	T_R	P_R	H^{o}, $\frac{cal}{g\text{-mole}}$	H, $\frac{cal}{g\text{-mole}}$	$(H^{o}-H_{P})_{T}$
1	403.1	7.76	0.857	0.235	8557.0	8064.2	492.8
2	443.1	14.56	0.942	0.441	10097.0	9362.4	734.6
3	462.0	21.50	0.982	0.651	10859.2	9878.4	980.8
4	402.0	7.89	0.855	0.239	8510.9	8021.0	489.8
5	367.6	4.42	0.781	0.134	7278.8	6910.5	368.3
6	403.1	7.76	0.857	0.235	8557.0	7963.4	593.6

Table 20. Comparison of Values Obtained From our Correlation For $(H^{o}-H_{P})_{T}/T_{c}$ for C_6H_6 and n-C_5H_{12}, with Values Calculated From the Joule-Thomson Data of Brown and Co-Workers (13, 14)

Run*	T_R	P_R	$(H^{o}-H_{P})_{T}/T_{c}$ Calculated	This Correlation	Hougen and Watson (41)	Hougen and Watson with York and Weber's Correction (36)	Watson and Smith (39)
			Benzene				
8	0.815	0.108	0.738	0.55	0.52	-	0.33
1	0.908	0.171	0.574	0.65	0.58	-	0.45
34	0.913	0.158	0.59	0.60	0.52	-	0.46
5	1.025	0.513	1.27	1.46	1.38	1.59	-
14	1.051	0.962	2.74	2.54	2.80	3.16	2.86
9	1.167	0.503	0.89	0.98	1.01	1.10	0.71
60	1.179	0.950	1.85	1.84	1.9	2.06	1.52
			n-Pentane				
5	0.781	0.134	0.78	0.785	0.8	-	0.63
4	0.855	0.239	1.035	1.11	1.1	-	0.86
1	0.857	0.235	1.05	1.13	1.1	-	0.87
6	0.857	0.235	1.26	1.13	1.1	-	0.87
2	0.942	0.441	1.56	1.58	1.7	-	1.41
3	0.982	0.651	2.08	-	1.2	-	-

*Numbers refer to designations of Lindsay and Brown, or Pattee and Brown.

Table 21. Comparison of Deviation from Observed Values of $(H^{\circ}-H_P)_T/T_c$ for Benzene and n-Pentane, Obtained from This Correlation, with Values Obtained from Other Correlations

Run	T_R	P_R	% Deviation from Observed			$\frac{(\text{Observed-Correlated})100}{\text{Observed}}$
			This Correlation	Hougen and Watson (52)	Hougen and Watson with Correction (49)	Watson and Smith (13)
				Benzene		
1	0.908	0.171	13.2	1.0	-	21.6
5	1.025	0.513	15.0	7.9	25.1	-
8	0.815	0.108	25.5	29.6	-	59.5
9	1.167	0.503	10.1	13.5	11.6	20.2
14	1.051	0.962	7.3	2.2	15.3	4.4
34	0.913	0.158	1.2	12.3	-	22.4
60	1.179	0.950	0.5	2.7	11.3	17.8
Average			11.8	9.9	15.8	24.3
				n-Pentane		
1	0.857	0.235	7.6	11.9	-	31.0
2	0.942	0.441	1.3	9.0	-	9.6
3	0.982	0.651	-	5.8	-	-
4	0.855	0.239	6.8	6.3	-	16.9
5	0.781	0.134	0.6	2.6	-	19.2
6	0.857	0.235	10.3	4.8	-	18.1
Average			5.3	6.7		19.0

CHAPTER VI

CONCLUSIONS

Isothermal changes in enthalpy have been calculated for carbon dioxide, nitrogen, benzene, and n-pentane, from the available adiabatic Joule-Thomson and C_p^o data, together with data for the second virial coefficient. These substances were chosen because at least a portion of the Joule-Thomson data extended into the vapor region below the critical temperature. An attempt was made to evaluate the second virial coefficient from P vs. T isenthalps for CO_2. While this is possible, in principle, it turned out that the Joule-Thomson data did not extend to sufficiently low pressures to permit the evaluation of this coefficient. It is hoped that future investigators will carry their Joule-Thomson measurements to pressures as low as one atmosphere, if possible, and will record data at intervals of a few atmospheres in the low pressure range.

A correlation of the quantity $(H^o-H)/T_c$ vs. P_R and T_R has been worked out for carbon dioxide and nitrogen using known values of this quantity for water as a reference. The correlation obtained represents the data below and above the critical better than existing correlations (3, 52), when results for the three substances, water, carbon dioxide, and nitrogen, are compared.

These three substances have widely different critical temperatures.

Comparison of values of $(H^o-H)/T_c$ for benzene and n-pentane, derived from Joule-Thomson measurements, showed only moderate agreement.

However, the predicted results compared favorably with those obtained from the Hougen and Watson correlation (52), and were in better agreement with observed values than those obtained from the correlation of Watson and Smith (3). It appears that, at least for some substances (H_2O, N_2, and CO_2) a correction function of the York and Weber type should be applied to existing correlation plots of $(H^o-H)/T_c$ vs. P_R and T_R for $T_R < 1$ and $P_R < P_V/P_c$ where P_V is the vapor pressure at T_R.

Further study of this and other correlation functions using more extensive $(H^o-H)/T_c$ data for these and other substances is needed.

APPENDIX

Table 22. Comparison of Joule-Thomson Coefficient of Roebuck, et al., for CO_2 (11) with Calculated Values of de Groot and Michels (8)

$$\% \text{ Difference} = \frac{(\mu_M - \mu_R)100}{\mu_R}$$

T, °C	de Groot and Michels	Roebuck, et al.	% Difference
	P = 1 Atmosphere		
25	1.001	1.066	-5.2
50	0.900	0.895	+0.6
100	0.667	0.649	+2.8
	P = 100 Atmospheres		
25	0.0715	0.0957	-25.3
50	0.643	0.5570	+15.4
100	0.552	0.5405	+ 2.0

Table 23. The Second Virial Coefficient of Carbon Dioxide

T, °K	B, $\frac{cc}{g\text{-mole}}$	Reference	T, °K	B	Reference
203.83	-330	(29)	273.15	-151	(33)
206.63	-316	(29)	300.00	-123	(33)
207.72	-313	(29)	325.00	-102	(33)
209.03	-302	(29)	350.00	- 85	(33)
210.12	-300	(29)	375.00	- 70	(33)
211.60	-286	(29)			
223.75	-226	(29)	298.15	-125.0	(30)
225.63	-229	(29)	304.19	-121.2	(30)
226.47	-225	(29)	313.15	-113.1	(30)
229.96	-212	(29)	323.15	-105.4	(30)
230.93	-216	(29)	348.15	- 88.4	(30)
231.79	-213	(29)	373.15	- 74.9	(30)
233.34	-210	(29)	398.15	- 63.1	(30)
235.06	-198	(29)	423.15	- 53.6	(30)
244.9	-175	(29)			
273.15	-142	(29)			

Method of calculation of B from data of Michels and de Groot (30) at 1 atmosphere.

$$PV = RT + BP$$

$$\frac{PV}{P_s V_s} = \frac{RT}{P_s V_s} + \frac{BP^*}{P_s V_s}$$

$$\frac{PV}{P_s V_s} = \frac{RT_s}{P_s V_s} \cdot \frac{T}{T_s} + \frac{BP}{P_s V_s}$$

$$\frac{PV}{P_s V_s} = A \text{ and } \frac{P_o V_o}{P_s V_s} = \frac{RT_s}{P_s V_s} = A_o$$

$$A = A_o \frac{T}{T_s} + \frac{BP}{P_s V_s}$$

$$B = \frac{P_s V_s}{P}\left(A - A_o \frac{T}{T_s}\right) = \frac{RT_s}{A_o P}\left(A - A_o \frac{T}{T_s}\right)$$

$$R = 0.08206 \ \frac{\text{l-atm}}{\text{g-mole-}^\circ\text{K}}$$

$$T_s = 273.15 \ ^\circ\text{K} \ (48)$$

$$A_o = 1.006824 \quad (48)$$

$$B = \frac{.08206 \cdot 273.15}{1.006824P}\left(A - \frac{1.006824T}{273.15}\right)$$

*Subscript refers to standard state.

Table 24. Numberical Differentiation of Second Virial Coefficient of CO_2 Difference Table

T	B	$\triangle_1$	$\triangle_2$	$\triangle_3$	$\triangle_4$			
205	-316							
		26				$\Delta_1 B_0$		
210	-290		-2				$\Delta_2 B_0$	
		24		0		$\Delta_1 B_1$		$\Delta_3 B_0$	
215	-266		-2		2		$\Delta_2 B_1$		$\Delta_4 B_0$
		22		+2		$\Delta_1 B_2$		$\Delta_3 B_1$	
220	-244		0		-12		$\Delta_2 B_2$		$\Delta_4 B_1$
		22		-10		$\Delta_1 B_3$		$\Delta_3 B_2$	
225	-222		-10		+20		$\Delta_2 B_3$		$\Delta_4 B_2$
		12		+10		$\Delta_1 B_4$		$\Delta_3 B_4$	
230	-210		0				$\Delta_2 B_4$		
		12				$\Delta_1 B_5$			
235	-198								

Newton's Formula (47): $$\frac{dB}{dT} = \frac{1}{h}\left[\Delta_1 B_o + (2p-1)\frac{\Delta_2 B_o}{2} + (3p^2-6p+2)\frac{\Delta_3 B_o}{6} + (4p^3-18p^2+2p-6)\frac{\Delta_4 B_o}{24} + (5p-40p^3+105p^2-100p+24)\frac{\Delta_5 B_o}{120} \cdots\right]$$

(Eq. 26)

$$p = \frac{t - t_o}{h} = \frac{t - 205.00}{5}$$

Values of $\frac{dB}{dT}$ for CO_2

Isenthalp	T, °K	$\frac{dB}{dT}$, $(\frac{cc}{°K})$ Graphical	Newton	Douglass-Avakian
II-10	208.64	5.10	5.04	
II-6	210.52	4.80	4.95	
I-9	211.55	4.70	4.53	
II-9	215.85	4.30	4.04	
II-5	550.52	3.55	3.40	4.00
II-1	231.98	2.40		2.30
I-8	272.21	1.00		1.05
I-6	320.19	0.65		0.62
I-4	402.05	0.42		0.42
I-3	470.64	0.40		
I-1	531.52	0.40		

Table 25. Zero Pressure Specific Heat of CO_2 (38)

$$\frac{C_p^o}{R} = 2.49405 + .0078669T - 4.27381 \times 10^{-6}T^2 \quad (180 - 600^oK)$$

Check of this equation:

T, ^oK	C_p^o Calc.		% Deviation
200	3.896	+.013	0.33
300	4.469	+.005	0.11
400	4.957	.000	0.00
500	5.359	+.006	0.11
600	5.676	.000	0.00
		Average	0.11%

$$C_p^o = 204.662 + 0.645558T - 3.507088 \times 10^{-4}T^2 \quad \frac{\text{cc-atm}}{\text{g-mole-}^oK} \text{ (Eq. 17)}$$

Calculation of C_p^o at final temperature for Joule-Thomson curves:

Isenthalp	T(Final)	$C_p^o(\frac{\text{cc-atm}}{\text{g-mole}^oK})$
I-1	531.52	448.7
I-3	470.64	430.8
I-4	402.05	407.5
I-6	320.19	375.5
I-8	272.21	354.4
I-9	211.55	325.6
II-1	231.98	335.6
II-5	220.52	330.1
II-6	210.52	325.1
II-9	215.85	327.7
II-10	208.64	324.1

Table 26. Calculation μ° For CO_2

$$\mu^{\circ} = \frac{-B + T\left(\frac{dB}{dT}\right)}{C_p^{\circ}}$$

Isenthalp	T, °K	B, $\frac{cc}{g\text{-mole}}$	C_p°, $\frac{cc\text{-atm}}{g\text{-mole-}^{\circ}K}$	$\frac{dB}{dT}$	$T\left(\frac{dB}{dT}\right)$	$T\left(\frac{dB}{dT}\right)-B$	μ°, $\frac{^{\circ}K}{atm}$	μ_f	$\mu_{avg.}$
II-10	208.64	-297*	324.1	5.04	1051.6	1349	4.16	3.50	2.56
II-6	210.52	-287*	325.1	4.95	1042.1	1329	4.09	3.25	2.58
I-9	211.55	-282*	325.6	4.53	958.3	1240	3.81	2.80	2.25
II-9	215.85	-262*	327.7	4.04	872.0	1134	3.46	3.30	2.74
II-5	220.52	-242*	330.1	3.40	749.8	992	3.01	3.00	2.71
II-1	231.98	-206**	335.6	2.30	533.6	740	2.21	2.55	2.00
I-8	272.21	-147**	354.4	1.05	285.8	433	1.22	1.25	1.20
I-6	320.19	-106**	375.5	0.62	198.5	305	0.81	1.00	0.92
I-4	402.05	- 63**	407.5	0.42	168.9	232	0.57	0.61	0.53

*By interpolation, using 5 terms of Newton's formula
** From graph
***Taken graphically at P_f
****Average value from last two quoted values of P and T

Table 27. Calculation of H for Isenthalps CO_2

Isenthalp	T (^oK)	$T\frac{dB}{dT} - B$ ($\frac{cc\text{-}atm}{g\text{-}mole\text{-}^oK}$)	P_f (atm)	$(H^o-H_P)_{T_f}$ ($\frac{cc\text{-}mole}{g\text{-}mole\text{-}^oK}$)	$(H^o-H_P)_T$ ($\frac{cal}{g\text{-}mole\text{-}^oK}$)	H^o ($\frac{cal}{g\text{-}mole\text{-}^oK}$)	H ($\frac{cal}{g\text{-}mole\text{-}^oK}$)
II-10	208.64	1349	1.5	2024	49.0	1348.5	1299.5
II-6	210.52	1329	2.0	2658	64.4	1363.4	1299.0
I-9	211.55	1240	1.9	2356	57.1	1371.5	1314.4
II-9	215.85	1134	1.6	1814	43.9	1405.5	1361.6
II-5	220.52	992	1.9	1884	45.6	1442.7	1397.1
II-1	231.98	740	1.9	1406	34.1	1535.0	1500.9
I-8	272.21	433	2.5	1083	26.1	1871.2	1845.0
I-6	320.19	305	4.6	1403	34.0	2295.4	2261.4
I-4	402.05	232	3.8	882	21.4	3072.1	3050.7

Table 28. Calculation of $(H^{\circ}-H_P)_T$ for CO_2

P_R	P Atm	Isenthalp	T, °C	T, °K	H° cal g-mole-°K	H cal g-mole-°K	$(H^{\circ}-H_P)_T$ cal g-mole-°K
0.10	7.3	II-9	-42.5	230.65	1514.9	1361.6	153.3
	7.3	II-5	-32.2	233.95	1551.0	1397.1	153.9
	7.3	II-1	-29.8	243.35	1620.2	1500.9	119.3
	7.3	I-8	+ 5.2	278.35	1904.2	1845.0	59.2
0.25	18.23	II-5	-18.8	254.4	1721.5	1397.1	324.4
	18.23	II-1	-11.0	262.2	1787.3	1500.9	286.4
	18.23	I-8	+18.0	291.2	2037.7	1845.0	192.7
	18.23	I-6	+59.8	333.0	2414.5	2261.4	153.1
	18.23	I-4	+137.0	410.2	3155.0	3050.7	104.3
0.50	36.45	II-10	3.8	277.0	1913.9	1299.5	614.4
	36.45	I-9	3.5	276.7	1911.3	1314.4	596.9
	36.45	II-9	7.8	281.0	1948.6	1361.6	587.0
	36.45	II-5	9.5	282.7	1962.8	1397.1	565.7
	36.45	II-1	14.7	287.9	2008.8	1500.9	507.9
	36.45	I-8	38.0	311.2	2215.7	1845.0	370.7
	36.45	I-6	74.1	347.3	2547.3	2261.4	285.9
	36.45	I-4	145.8	419.0	3240.7	3050.7	190.0
0.75	54.68	II-10	25.0	298.2	2097.9	1299.5	798.4
	54.68	II-6	24.8	298.0	2096.1	1299.0	797.1
	54.68	I-9	24.5	297.7	2093.4	1314.0	779.0
	54.68	II-9	29.6	302.8	2138.8	1361.6	777.2
	54.68	II-5	31.0	304.2	2151.3	1397.1	754.2
	54.68	II-1	36.0	309.2	2196.0	1500.9	695.1
	54.68	I-8	54.5	327.7	2363.9	1845.0	518.9
	54.68	I-6	87.5	360.7	2671.8	2261.4	410.4
	54.68	I-4	153.8	427.0	3321.1	3050.7	270.4
1.00	72.9	I-9	42.0	315.2	2250.1	1314.4	935.7
	72.9	I-8	69.0	342.2	2497.9	1845.0	652.9
	72.9	I-6	98.2	371.4	2773.9	2261.4	512.5
	72.9	I-4	161.6	434.8	3399.9	3050.7	349.2
1.25	91.13	I-9	57.0	330.2	2386.8	1314.4	1072.4
	91.13	I-8	81.2	354.4	2612.2	1845.0	767.2
	91.13	I-6	108.5	381.7	2873.2	2261.4	611.8
	91.13	I-4	169.0	442.2	3475.2	3050.7	424.5
1.50	109.35	I-9	67.8	341.0	2486.7	1314.4	1172.3
	109.35	I-8	90.2	363.4	2697.4	1845.0	852.4
	109.35	I-6	117.8	391.0	2963.7	2261.4	702.3
	109.35	I-4	175.6	448.8	3542.8	3050.7	492.1

Table 28. Calculation of $(H^{o}-H_{p})_{T}$ for CO_2 (cont'd)

P_R	P Atm	Isenthalp	T, °C	T, °K	H^{o} cal/g-mole-°K	H cal/g-mole-°K	$(H^{o}-H_{p})_{T}$ cal/g-mole-°K
1.75	127.58	I-9	76.7	349.9	2569.9	1314.4	1255.5
	127.58	I-8	98.3	371.4	2774.9	1845.0	929.9
	127.58	I-6	126.2	399.4	3046.0	2261.4	784.6
	127.58	I-4	181.6	454.8	3604.6	3050.7	553.9
2.00	145.80	I-9	85.0	358.2	2648.1	1314.4	1333.7
	145.80	I-8	106.1	379.3	2850.0	1845.0	1005.0
	145.80	I-6	133.3	406.5	3116.1	2261.4	854.7
	145.80	I-4	187.3	460.5	3663.5	3050.7	612.8
2.50	182.25	I-9	98.0	371.2	2771.9	1314.4	1457.5
	182.25	I-8	120.8	394.0	2993.0	1845.0	1148.0
	182.25	I-6	145.5	418.7	3237.6	2261.4	976.2
	182.25	I-4	197.5	470.7	3769.5	3050.7	718.8

Table 29. Comparison of Enthalpy Differences From Table 10 with Values Given by Michels (50) and by Sweigert, et al. (51)

Comparison with Data of Michels

$T_R \rightarrow$	1.1			1.2			1.3**			1.4**		
P_R	Table 10	Michels	Deviation*	Table 10	Michels	Deviation*	Table 10	Michels	Deviation*	Table 10	Michels	Deviation*
0.25	149	136	+9.6	124	111	+11.7	115	100	+15.0	-	86	-
0.50	310	290	+6.9	255	237	+ 7.6	195	204	- 4.4	-	174	-
0.75	487	470	+2.8	396	381	+ 3.9	320	314	+ 1.9	273	266	+3.8
1.00	702	702	0.0	540	536	- 0.7	433	429	+ 0.9	365	360	+1.4
1.25	994	985	+0.9	690	698	- 1.1	555	552	+ 0.5	470	454	+3.5
1.50				850**	874	- 2.8	680**	675	+ 0.7	565**	550	+2.7
1.75				975**	1060	- 8.0	795**	800	- 0.6	660**	650	+1.5
2.00				1130**	1248	- 9.6	900**	925	- 2.8	755**	746	+1.2

Average Deviation = 4.52% in range used in correlation
3.95% overall including $T_R > 1.3$, $P_R > 1.25$

Comparison with Data of Sweigert, et al.

The enthalpy at the low pressure end of each isenthalp has been identified by interpolation from the tables of Sweigert, et al. The value so obtained for each isenthalp has been subtracted from the enthalpy calculated, for isenthalp I-4. This has been repeated, using enthalpies from Table 27.

Isenthalp	H_4-H_i		
	Table 27	Sweigert	% Deviation*
II-10	1751.2	1775	-1.3
II-6	1751.7	1770	-1.0
II-9	1736.3	1750	-0.8
II-9	1689.1	1715	-1.5
II-5	1653.6	1675	-1.3
I-1	1549.8	1575	-1.6
I-8	1205.7	1225	-1.6
I-6	789.3	825	-1.3
I-4	0	0	
Average Deviation =			-1.3%

*% Deviation = $\frac{(\text{Table 29} - \text{Michels})100}{\text{Michels}}$ or $\frac{(\text{Table 27} - \text{Sweigert})100}{\text{Sweigert}}$

**Values taken from graph not shown in this work.

Table 30. The Second Virial Coefficient of Nitrogen

T, °K	B, $\frac{cc}{g\text{-mole}}$ Friedman, et al. (32)	Bloomer and Rao (31)	Beattie and Bridgeman (33)	Keyes (34)
74.28		-286.6		
77.61		-270		
80.00	-252			
83.17		-245		
88.72		-214		
90.00	-205			
94.28		-193		
99.83		-180		
100.00	-162.5			
105.44		-165		
110.00	-128			
110.94		-134		
116.50		-126		
120.00	-102			
122.06		-118		
127.61		-107		
133.16			-90.3	-94.0
133.17		- 96		
138.72		- 84		
143.16			-78.3	
144.28		- 70		
153.16			-68.2	-68.7
173.16			-52.3	-51.5
198.16			-37.6	
223.16			-26.7	
248.16			-18.3	
273.16			-11.6	
298.16			- 6.1	
323.16			- 1.5	
348.16			+ 2.4	
373.16			+ 5.7	
398.16			+ 8.7	
423.15		11.2		
448.15		13.4		
473.15		15.4		15.2
498.15		17.2		
523.15		18.4		
548.15		20.3		
573.15		21.7		20.8
598.15		22.9		
623.15		24.0		
648.15		25.0		
683.15		26.0		

Table 31. Numerical Differentiation of the Second Virial Coefficient of Nitrogen Difference Table

T, °K	B, $\frac{cc}{g\text{-mole}}$	Δ_1	Δ_2	Δ_3	Δ_4	Δ_5
75	-286					
		31				
80	-255		-4			
		27		+1		
85	-228		-3		-2	
		24		-1		+5
90	-204		-4		+3	
		20		+2		
95	-184		-2			
		18				
100	-166					

Differentiation by Douglass-Avakian Formula

T, °K	B, $\frac{cc}{mole}$	k	ky	k^3y
282.20	-9	-3	+27	+243
287.20	-8	-2	+16	+ 64
292.20	-7	-1	+ 7	+ 7
297.20		0	-	-
302.20	-5	1	- 5	- 5
307.20	-4	2	- 8	- 32
312.20	-3	3	- 9	- 81
			+28	+196

$$\frac{dB}{dT} = 397\ \frac{ky}{1512} - \frac{7\ k^3y}{216\ h} = 0.1945$$

Values of B and $\frac{dB}{dT}$ at T_f

Isenthalp	T_f, °K	P_f, Atm.	$\frac{dB}{dT}$ at T_f		$\frac{\Delta B}{\Delta T}$
			Numerical	Method Used	
1	99.70	1.45	4.16	Newton	3.6
2	86.98	1.55	5.68	Newton	4.8
3	83.35	1.65	5.84	Newton	5.4
5	81.40	1.32	5.96	Newton	5.4
7	297.20	2.6	0.19	Douglass-Avakian	0.2
8	234.58	1.5	0.353	Douglass-Avakian	0.4
9	266.36	3.2	0.264	Douglass-Avakian	0.2
10	164.25	1.5	0.754	Douglass-Avakian	0.8
11	126.89	2.4	1.683	Douglass-Avakian	1.6
12	356.27	4.5	0.136	Douglass-Avakian	0

Table 32. Zero Pressure Specific Heat of N_2 (37)

$C_p^o = 6.954131 - 7.6151 \times 10^{-5}T + 3.2725 \times 10T^2$ $\frac{cal}{g\text{-mole-}^oK}$ (eq. 18) (70-400°K)

Equation derived by method of selected points

T, °K	C_p^o, Observed	C_p^o, Calculated	$\triangle$	% Deviation
100.00	6.95	6.95	.00139	.02
155.57	6.95	6.95	.00141	.02
200.00	6.95	6.95	.00000	.00
255.55	6.95	6.96	.00294	.04
305.56	6.96	6.96	.00447	.06
361.11	6.97	6.97	.00001	.00
388.88	6.98	6.97	.00634	.09
99.70	6.95	6.95	.00139	.02
86.98	6.95	6.95	.00111	.02
83.35	6.95	6.95	.00101	.01
74.92	6.95	6.95	.00075	.01
81.40	6.95	6.95	.00095	.01
120.38	6.95	6.95	.00162	.02

Average Deviation = 0.025%

Table 33. Calculation of μ° for Nitrogen

$$\mu^\circ = \frac{T\frac{dB}{dT} - B}{C_p^\circ}$$

Isenthalp	T, °K	$\frac{dB}{dT}$, $\frac{cc}{°K}$	B $\frac{cc}{g\text{-mole}}$	C_p° $\frac{cc\text{-atm}}{g\text{-mole}}$ °K	$T\frac{dB}{dT} - B$	μ°	μ Avg.*
1	99.70	4.16	-167	287.0	581.8	2.027	1.6
2	86.98	5.68	-218	287.0	712.1	2.481	1.85
3	83.35	5.84	-236	287.0	722.8	2.518	2.2
5	81.40	5.96	-247	287.0	732.1	2.551	1.85
7	297.20	0.19	- 6	287.2	62.5	0.218	.21
8	234.58	0.353	- 22	287.1	104.8	0.288	.33
9	266.36	0.264	- 13	287.1	83.3	0.245	.27
10	164.25	0.754	- 62	287.1	185.3	0.647	.71
11	126.89	1.683	-100	287.0	313.6	1.093	.93
12	356.27	0.136	+ 4	287.7	44.5	0.155	.14

Comparison of some of these values for μ° with values reported by Michels (9) in this temperature range.

		μ°		
Isenthalp	T, °K	Table 33	Michels	% Difference $(\frac{M-(33)}{M})100$
7	297.20	0.218	0.225	3.1
8	234.58	0.288	0.288	0.0
9	266.36	0.245	0.245	0.0
10	164.25	0.647	0.671	3.7
12	356.27	0.155	0.154	0.6
			Average =	1.5%

*$\frac{\Delta T}{\Delta P}$ taken between two lowest temperatures and pressures

Table 34. Calculation of H for Isenthalps of Nitrogen

H = 0 When T = 0

$$H_T^o = \int_o^T C_p^o dT = 6.954131T - 3.80755 \times 10^{-5}T^2 + 1.09083 \times 10^{-7}T^3 \ \frac{cal}{g\text{-mole-}^oK} \text{ (Eq. 22) } (70\text{-}400^oK)$$

$$H_T^o - H_T^{P_f} = (T\frac{dB}{dT} - B)P_f$$

$$H_T^o - (H_T^o - H_T^{P_f}) = H_T^P$$

Isenthalp	T_f, °K	P_f, Atm.	$(T\frac{dB}{dT} - B)$, cc	$(H^o-H_P)_T$ $\frac{cc}{atm\text{-}g\text{-}mole}$	$(H^o-H_P)_{T_f}$ $\frac{cal}{g\text{-}mole}$	H^o	H
1	99.70	1.45	581.8	843.6	20.43	693.06	672.6
2	86.98	1.548	712.1	1102.3	26.70	604.65	578.0
3	83.35	1.645	722.8	1189.0	28.80	579.43	550.6
5	81.40	1.32	732.1	966.4	23.40	565.88	542.5
7	297.20	2.6	62.5	162.5	3.94	2066.27	2062.3
8	234.58	1.5	104.8	157.2	3.81	1630.61	1626.8
9	266.36	3.2	83.3	266.6	6.46	1851.66	1845.2
10	164.25	1.5	185.8	278.7	6.75	1141.67	1134.9
11	126.89	2.4	313.6	752.6	18.23	882.02	863.8
12	356.27	4.5	44.5	200.3	4.85	2477.65	2472.8

Table 35. Calculation of $(H^{o}-H_{P})_{T}$ for Nitrogen

P_R	P, Atm.	Isenthalp	T, °K	H^{o} cal/g-mole	H cal/g-mole	$(H^{o}-H_{P})_{T}$ cal/g-mole
0.10	3.35	1	103.86	722.0	672.6	49.4
		7	297.36	2067.4	2062.3	5.1
		10	165.66	1151.5	1134.9	16.6
0.25	8.385	1	112.2	779.9	672.6	107.3
		7	298.5	2076.3	2062.3	14.0
		8	236.8	1646.1	1626.8	19.3
		9	267.7	1860.9	1845.2	15.7
		10	168.8	1173.3	1134.9	38.4
		11	132.4	920.3	863.8	56.5
		12	356.7	2480.6	2472.8	7.8
0.50	16.77	1	123.2	856.4	672.6	183.8
		7	300.3	2087.9	2062.3	25.6
		8	239.5	1664.8	1626.8	38.0
		9	269.8	1875.6	1845.2	30.4
		10	173.7	1207.4	1134.9	72.5
		11	140.2	974.5	863.8	110.7
		12	357.9	2489.0	2472.8	16.2
0.596	20.00	1	126.7	880.7	672.6	208.1
		2	117.2	814.7	578.0	236.7
		3	116.7	811.2	550.6	260.6
		5	116.3	808.4	542.5	265.9
		7	301.0	2092.7	2062.3	30.4
		8	240.7	1673.2	1626.8	46.4
		9	270.7	1881.5	1845.2	36.3
		10	175.4	1219.2	1134.9	84.3
		11	142.9	993.3	863.8	129.5
		12	358.5	2492.9	2472.8	20.1
0.75	25.155	1	131.8	916.1	672.6	243.5
		2	123.3	857.1	578.0	279.1
		3	122.3	850.1	550.6	299.5
		5	121.8	846.6	542.5	304.1
		7	302.1	2100.4	2062.3	38.1
		8	242.3	1684.3	1626.8	57.5
		9	272.1	1891.6	1845.2	46.4
		10	178.2	1238.7	1134.9	103.8
		11	146.9	1021.1	863.8	157.3
		12	359.2	2498.1	2472.8	25.3

Table 35. Calculation of $(H^{o}-H_{P})_{T}$ for Nitrogen (cont'd)

P_R	P, Atm.	Isenthalp	T, °K	H^{o} cal/g-mole	H cal/g-mole	$(H^{o}-H_{P})_{T}$ cal/g-mole
1.00	33.54	1	138.4	962.1	672.6	289.5
		2	131.4	913.4	578.0	335.4
		3	130.7	908.5	550.6	357.9
		5	129.2	898.1	542.5	355.6
		7	303.6	2112.2	2062.3	49.9
		8	244.9	1702.4	1626.8	75.6
		9	274.1	1905.5	1845.2	60.3
		10	181.4	1260.9	1134.9	126.0
		11	152.8	1062.1	863.8	198.3
		12	360.2	2505.4	2472.8	32.6
1.25	41.925	1	144.4	1003.7	672.6	331.1
		2	138.0	959.2	578.0	381.2
		3	137.3	954.4	550.6	403.8
		5	135.2	939.8	542.5	397.3
		7	305.0	2120.6	2062.3	58.3
		8	247.3	1719.1	1626.8	92.3
		9	276.0	1918.7	1845.2	73.5
		10	186.3	1294.9	1134.9	160.0
		11	158.2	1099.6	863.8	235.8
		12	361.2	2512.0	2472.7	39.3
1.50	50.31	1	149.7	1040.6	672.6	368.0
		2	143.9	1000.2	578.0	422.2
		3	142.9	993.3	550.6	442.7
		5	141.2	981.6	542.5	439.1
		7	306.6	2131.7	2062.3	69.4
		8	249.7	1735.8	1626.8	109.0
		9	278.0	1932.7	1845.2	87.5
		10	190.1	1321.4	1134.9	186.5
		11	163.2	1134.4	863.8	270.6
		12	362.2	2519.0	2472.7	46.3
1.75	58.695	1	154.0	1070.4	672.6	397.8
		2	148.5	1032.2	578.0	454.2
		3	147.5	1025.3	550.6	474.7
		5	146.2	1016.2	542.5	473.7
		7	308.0	2141.5	2062.3	79.2
		8	251.8	1750.4	1626.8	123.6
		9	279.7	1944.5	1845.2	99.3
		10	193.3	1343.6	1134.9	208.7
		11	167.7	1165.7	863.8	301.9
		12	363.2	2525.9	2472.8	53.1

Table 35. Calculation of $(H^o-H_p)_T$ for Nitrogen (cont'd)

P_R	P, Atm.	Isenthalp	T, °K	H^o $\frac{cal}{g\text{-mole}}$	H $\frac{cal}{g\text{-mole}}$	$(H^o-H_p)_T$ $\frac{cal}{g\text{-mole}}$
2.00	67.08	1	158.1	1098.9	672.6	426.3
		2	152.9	1062.7	578.0	484.7
		3	151.8	1055.0	550.6	504.4
		5	150.7	1047.5	542.5	505.0
		7	309.3	2150.5	2062.3	88.2
		8	253.7	1763.6	1626.8	136.8
		9	281.5	1957.0	1845.2	111.8
		10	196.4	1365.2	1134.9	230.3
		11	171.7	1193.5	863.8	329.7
		12	364.1	2532.3	2472.8	59.5
2.50	83.85	1	164.2	1141.3	672.6	468.7
		2	160.2	1113.5	578.0	535.5
		3	157.7	1096.2	550.6	545.6
		5	156.9	1090.4	542.5	547.9
		7	311.7	2167.2	2062.3	104.9
		8	257.3	1788.6	1626.8	161.8
		9	284.5	1979.9	1845.2	134.7
		10	201.9	1403.4	1134.9	268.5
		11	177.9	1236.6	863.8	372.8
		12	365.7	2543.4	2472.8	70.6

Table 36. Comparison of Enthalpy Differences from Table 35 with Values Given by Lunbeck, et al., (9) and by Bloomer and Rao (31)

T, °K	$(H^o-H_p)_T$ cal/g-mole, at 50 Atm.		
	Lunbeck	This Paper	% Deviation
148	385.6	370	4.2
173	245.4	235	4.3
198	183.0	170	7.6
223	141.2	134.2	5.1
273	89.1	90	0.8
323	60.2	60	0.1
348	49.8	50	0.2
		Average =	3.0%

Comparison of Enthalpy Difference Between Isenthalps from Tables of Bloomer and Rao (31), and from Table 34

Isenthalp	$(H_{12}-H_i)$, cal/g-mole*		
	Bloomer	This Paper	% Deviation
1	1795	1800.2	0.40
2	1898	1894.1	0.15
3	1922	1922.2	0.00
5	1940	1930.3	0.52
7	415	410.5	1.10
8	825	846.0	2.50
9	620	627.6	1.00
10	1330	1337.9	0.60
11	1605	1609.0	0.30
		Average =	0.73%

*$(H_{12} - H_i)$ = the enthalpy of isenthalp 12 less the enthalpies of the other isenthalps.

Table 37. Estimate of Error in Calculation of $(H^{o}-H_{P})_{T}$ for N_2 and CO_2: (a) Nitrogen

Isenthalp	T_f	-B	-.05B	$(\frac{dB}{dT})$ at P_f	$T_f(\frac{dB}{dT})$	.05 $T_f(\frac{dB}{dT})$	P_f	(.05 $T\frac{dB}{dT}$ - .05B) $\frac{cc}{g\text{-mole}}$	P_f x (.05$T\frac{dB}{dT}$ - .05B) cal
1	99.70	167	8.4	4.16	415	20.8	1.45	29.2	1.02
2	86.98	218	10.9	5.68	492	24.6	1.548	35.5	1.32
3	83.35	236	11.8	5.84	487	24.4	1.645	36.2	1.44
5	81.40	247	12.3	5.98	485	24.2	1.32	36.5	1.17
7	297.20	6	0.3	0.19	56	2.8	2.6	3.1	0.20
8	234.58	22	1.0	0.353	83	4.1	1.5	5.1	0.18
9	266.36	13	0.7	0.264	68	3.0	3.2	3.7	0.29
10	164.25	62	3.0	0.754	124	6.0	1.5	9.0	0.33
11	126.89	100	5.0	1.683	214	10.7	2.4	15.7	0.92
12	356.27	4	0.3	0.136	48	2.4	4.5	2.7	0.31

Isenthalp	P_R	$H^{o}-H$, cal	Estimated Error, cal	% Error
1	0.10	49.4	1.02	2.1
7		5.1	0.20	3.9
10		16.6	0.33	2.0
1	0.25	107.3	1.02	1.1
7		14.0	0.20	0.7
8		19.3	0.18	0.9
9		15.7	0.29	1.9
10		38.4	0.33	0.9
11		56.5	0.92	1.6
12		7.8	0.31	4.0
1	0.75	243.5	1.02	0.4
2		279.1	1.32	0.5
3		299.5	1.44	0.5
5		304.1	1.17	0.3
7		38.1	0.20	0.5

Table 37. Estimate of Error in Calculation of $(H^{\circ}-H_P)_T$ for N_2 and CO_2 (cont'd): (a) Nitrogen

Isenthalp	P_R	$H^{\circ}-H$, cal	Estimated Error, cal	% Error
8	0.75	57.5	0.18	0.3
9		46.4	0.29	0.6
10		103.8	0.33	0.3
11		157.3	0.92	0.6
12		25.3	0.31	1.2
1	1.25	331.1	1.02	0.3
2		381.2	1.32	0.3
3		403.8	1.44	0.4
5		397.3	1.17	0.3
7		58.3	0.20	0.3
8		92.3	0.18	0.2
9		73.5	0.29	0.4
10		160.0	0.33	0.2
11		235.8	0.92	0.4
12		39.3	0.31	0.8
			Average =	0.93%

Table 37. Estimate of Error in Calculation of $(H^{\circ}-H_P)_T$ for N_2 and CO_2 (cont'd) (b) Carbon Dioxide

Isenthalp	T_f	-B	-.05B	$(\frac{dB}{dT})$ at P_f	$T_f(\frac{dB}{dT})$	.05 $T_f(\frac{dB}{dT})$	P_f	(.05 $T\frac{dB}{dT}$ - .05B)$\frac{cc}{g\text{-mole}}$	P_f x (.05$T\frac{dB}{dT}$ - .05B) cal
II-10	208.64	297	14.9	5.04	1051.6	52.6	1.5	67.5	2.4
II-6	210.52	287	14.4	4.95	1042.1	52.1	2.0	66.5	3.2
I-9	211.55	282	14.1	4.53	958.3	47.9	1.9	62.0	2.8
II-9	215.85	262	13.1	4.04	872.0	43.6	1.6	56.7	2.2
II-5	220.52	242	12.1	3.40	749.8	38.0	1.9	50.1	2.3
II-1	231.98	206	10.3	2.30	533.6	26.7	1.9	37.0	1.7
II-8	272.21	147	7.4	1.05	285.8	14.8	2.5	23.2	1.4
I-6	320.19	106	5.3	0.62	198.5	10.0	4.6	15.3	1.7
I-4	402.05	63	3.0	0.42	168.9	8.4	3.8	6.8	0.6

Isenthalp	P_R	$H^{\circ}-H$, cal	Estimated Error, cal	% Error
II-9	0.10	153.3	2.2	1.4
II-5		153.9	2.3	1.5
II-1		119.3	1.7	1.4
I-8		59.2	1.4	2.4
II-5	0.25	324.4	2.3	0.7
II-1		286.4	1.7	0.6
I-8		192.7	1.4	0.7
I-6		153.1	1.7	0.9
I-4		104.3	0.6	0.6
II-10	0.75	798.4	2.4	0.3
II-6		797.1	3.2	0.4
I-9		779.0	2.8	0.4
II-9		777.2	2.2	0.3
II-5		754.2	2.3	0.3
II-1		695.1	1.7	0.2

Table 37. Estimate of Error in Calculation of $(H^{o}-H_{P})_{T}$ for N_2 and CO_2 (cont'd): (b) Carbon Dioxide

Isenthalp	P_R	$H^{o}-H$, cal	Estimated Error, cal	% Error
II-8	0.75	518.9	1.4	0.3
I-6		410.4	1.7	0.4
I-4		270.4	0.6	0.5
I-9	1.25	1072.4	2.8	0.3
I-8		767.2	1.7	0.2
I-6		611.8	1.7	0.3
I-4		424.5	0.6	0.1
			Average =	0.65% error

Error in reading pressure has been estimated to lead to error of 1.5% in $(H^{o}-H_{P})_{T}$. The total error, therefore, is about 2.4% for N_2, and 2.2% for CO_2.

Table 38. The Enthalpy of Steam (12)

	T, °F	T, °K	H, BTU/lb	H, $\frac{cal^*}{g\text{-mole}}$
P_R = 0.10	430	494.22	1208.2	12,092.5
P = 21.82 Atm. = 320.66 psia	480	522.06	1242.6	12,436.8
	520	544.27	1267.4	12,685.0
	580	577.60	1302.0	13,031.3
	640	610.94	1335.0	13,361.6
	700	644.27	1367.2	13,790.9
P_R = 0.25	520	544.27	1200.2	12,012.4
P = 54.54 Atm. = 801.55 psia	580	577.60	1255.0	12,560.9
	640	610.94	1299.3	13,004.3
	700	644.27	1338.5	13,396.6
	860	733.16	1432.8	14,304.4
	1000	810.94	1511.0	15,123.1
	1100	866.49	1566.2	15,675.6
	1200	922.05	1621.4	16,228.0
	1400	1033.16	1733.2	17,347.0
	1600	1144.27	1847.5	18,491.0
P_R = 0.50	610	594.27	1170.7	11,719.1
P = 109.08 Atm. = 1603.1 psia	640	610.94	1214.8	12,158.5
	670	627.61	1249.0	12,500.8
	700	644.27	1278.4	12,795.1
	860	733.16	1399.4	14,006.1
	1000	810.94	1486.9	14,881.9
	1200	922.05	1604.5	16,058.9
	1400	1033.16	1720.5	17,219.9
	1600	1144.27	1837.5	18,390.9
P_R = 0.75	670	627.61	1126.9	11,278.8
P = 163.63 Atm. = 2404.65 psia	690	638.72	1172.8	11,738.2
	700	644.27	1190.8	11,918.3
	860	733.16	1361.4	13,625.8
	1000	810.94	1461.6	14,628.7
	1200	922.05	1587.3	15,886.8
	1400	1033.16	1707.6	17,090.8
	1600	1144.27	1827.3	18,288.8
P_R = 1.00	705.40	647.27	902.7	9,034.8
P = 218.16 Atm. = 3206.2 psia	790	694.27	1237.2	12,328.7
	860	733.16	1317.9	13,190.4
	1000	810.94	1434.7	14,359.4
	1200	922.05	1569.8	15,711.6
	1400	1033.16	1694.6	16,960.7
	1600	1144.27	1817.2	18,187.7

*International calorie

Table 38. The Enthalpy of Steam (12) (Cont'd)

	T, °F	T, °K	H, BTU/lb	H, $\frac{cal}{g\text{-}mole}$*
P_R = 1.25	710	649.83	787.1	7,877.8
P = 272.71 Atm. = 4007.8 psia	790	694.27	1152.8	11,538.0
	860	733.16	1267.3	12,684.0
	1000	810.94	1406.5	14,077.2
	1200	922.05	1551.9	15,532.4
	1400	1033.16	1681.6	16,830.6
	1600	1144.27	1807.1	18,086.6
P_R = 1.50	710	649.83	667.8	6,683.8
P = 327.24 Atm. = 4809.3 psia	790	694.27	1037.0	10,379.0
	860	733.16	1208.8	12,098.5
	1000	810.94	1376.7	13,778.9
	1200	922.05	1533.9	15,352.3
	1400	1033.16	1668.4	16,698.4
	1600	1144.27	1796.9	17,984.6

* International calorie

Table 39. Zero Pressure Enthalpy of Steam (39)

Keyes' equation for H^o is:

$$H^o = 1.4722\,(T-T_o) + 3.8863 \times 10\,(T^2-T_o^2) + 110.16 \log_{10}\frac{T}{T_o} - 9.49 \times 10^{-9}\,(T^3-T_o^3) + 2501.09 \ \frac{\text{joules}}{g}$$

$$(T_o = 273.16\ ^oK)$$

T, ^oK	H^o, $\frac{\text{joule}}{g}$	H^o $\frac{\text{cal}}{\text{g-mole}}$ *
773.16	3486.09	15,013.0
544.27	3017.99	12,997.1
577.60	3084.13	13,282.0
610.94	3150.97	13,569.8
644.27	3218.47	13,860.5
733.16	3401.88	14,650.4
810.94	3566.57	15,359.6
866.49	3686.63	15,876.7
922.05	3808.75	16,402.6
1033.16	4058.66	17,478.9
1144.27	4317.90	18,595.3
594.27	3117.47	13,425.6
627.61	3184.40	13,713.8
638.72	3207.18	13,811.9
647.27	3224.57	13,886.8
649.83	3229.78	13,909.2
694.27	3321.03	14,302.2
494.28	2909.3	12,528.9
522.06	2974.1	12,808.0

*Defined calories

Table 40. Calculation of $(H^{\circ}-H_P)_T$ for Steam

(1 International calorie = 1.000652 Defined calorie)

P_R	P, Atm.	T, °K	H°, cal* / g-mole	H, cal* / g-mole	$(H^{\circ}-H_P)_T$, cal* / g-mole
0.10	21.82	494.22	12,528.9	12,100.2	428.7
		522.06	12,808.6	12,444.7	363.9
		544.27	12,997.1	12,693.1	304.0
		577.60	13,282.0	13,039.7	242.3
		610.94	13,569.8	13,370.1	199.7
		644.27	13,860.5	13,799.7	60.8
0.25	54.54	544.27	12,997.1	12,020.0	977.1
		577.60	13,282.0	12,568.9	713.1
		610.94	13,569.8	13,012.6	557.2
		644.27	13,860.5	13,405.1	455.4
		733.16	14,650.4	14,349.5	300.9
		810.94	15,359.6	15,132.7	226.9
		866.49	15,876.7	15,685.5	191.2
		922.05	16,402.6	16,238.3	164.3
		1033.16	17,478.9	17,358.0	120.9
		1144.27	18,595.3	18,502.7	92.6
0.50	109.08	594.27	13,425.6	11,726.6	1699.0
		610.94	13,569.8	12,166.2	1403.6
		627.61	13,713.8	12,508.7	1205.1
		644.27	13,860.5	12,803.3	1057.2
		733.16	14,650.4	14,015.0	635.4
		810.94	15,359.6	14,891.4	468.2
		922.05	16,402.6	16,069.1	333.5
		1033.16	17,478.9	17,230.8	248.1
		1144.27	18,595.3	18,402.6	192.7
0.75	163.63	627.61	13,713.8	11,286.0	2427.8
		638.72	13,811.9	11,745.6	2066.3
		644.27	13,860.5	11,925.8	1934.7
		733.16	14,650.4	13,634.4	1016.0
		810.94	15,359.6	14,638.0	721.6
		922.05	16,402.6	15,896.9	505.7
		1033.16	17,478.9	17,101.6	377.3
		1144.27	18,595.3	18,299.6	295.3

*Defined calorie

Table 40. Calculation of $(H^{o}-H_{P})_{T}$ for Steam (cont'd)

P_R	P, Atm.	T, °K	H^{o}, cal* / g-mole	H, cal* / g-mole	$(H^{o}-H_{P})_{T}$ cal* / g-mole
1.00	218.16	647.27	13,860.5	9,040.5	4,820.0
		694.27	14,302.2	12,390.6	1,911.6
		733.16	14,650.4	13,198.8	1,451.6
		810.94	15,359.6	14,368.1	991.0
		922.05	16,402.6	15,721.6	681.0
		1033.16	17,478.9	16,971.5	507.4
		1144.27	18,595.3	18,199.2	396.1
1.25	272.71	649.83	13,909.2	7,882.8	6,026.4
		694.27	14,302.2	11,545.3	2,756.9
		733.16	14,650.4	12,692.1	1,958.3
		810.94	15,359.6	14,086.1	1,273.5
		922.05	16,402.6	15,542.6	860.0
		1033.16	17,478.9	16,841.3	637.6
		1144.27	18,595.3	18,098.1	497.2
1.50	327.24	649.83	13,909.2	6,688.0	7,221.2
		694.27	14,302.2	10,385.6	3,916.6
		733.16	14,650.4	12,106.2	2,544.2
		810.94	15,359.6	13,787.6	1,572.0
		922.05	16,402.6	15,362.1	1,040.5
		1033.16	17,478.9	16,709.0	769.9
		1144.27	18,595.3	17,996.0	599.3

*Defined calorie

Table 41. Calculation of the Exponent in the Correction Factor, $\left(\frac{T_{c_i}}{T_{c_w}}\right)^n$

(a) Carbon Dioxide

T_R	P_R	A $\left(\frac{(H^\circ-H_P)_T}{T_c}\right)_{H_2O}$	B $\left(\frac{(H^\circ-H_P)_T}{T_c}\right)_{CO_2}$	C $\frac{B}{A}$	D log C	E $n = \frac{D}{\log 0.471}$
0.80	0.10	0.569	0.394	0.694	-0.1586	0.485
0.85	0.10	0.464	0.292	0.632	-0.1993	0.611
0.90	0.10	0.371	0.213	0.575	-0.2403	0.738
0.95	0.10	0.300	-	-	-	-
0.85	0.25	1.412	0.993	0.702	-0.1537	0.471
0.90	0.25	1.065	0.812	0.762	-0.1180	0.362
0.95	0.25	0.843	0.690	0.819	-0.0867	0.265
1.00	0.25	0.711	0.608	0.853	-0.0691	0.212
1.10	0.25	0.506	0.490	0.968	-0.0141	0.043
1.20	0.25	0.394	0.407	1.035	+0.0149	-0.046
0.95	0.50	2.085	1.629	0.782	-0.1068	0.326
1.00	0.50	1.604	1.305	0.814	-0.0894	0.274
1.10	0.50	1.089	1.018	0.935	-0.0292	0.090
1.20	0.50	0.805	0.839	1.042	+0.0178	-0.054
1.00	0.75	2.910	2.370	0.815	-0.0888	0.369
1.10	0.75	1.785	1.600	0.898	-0.0467	0.143
1.20	0.75	1.277	1.300	1.018	+0.0077	-0.023
1.00	1.00	7.46	-	-	-	
1.10	1.00	2.57	2.305	0.900	-0.0458	0.140
1.20	1.00	1.785	1.775	0.995	-0.0022	0.007
1.00	1.25	-	-	-	-	
1.10	1.25	3.51	3.258	0.928	-0.0325	0.100
1.20	1.25	2.335	2.265	0.972	-0.0123	0.038

Table 41. Calculation of the Exponent in the Correction Factor, $\left(\frac{T_{c_i}}{T_{c_w}}\right)^n$ (cont'd)

(b) Nitrogen

T_R	P_R	A $\left(\frac{(H^\circ-H_P)_T}{T_c}\right)_{H_2O}$	B $\left(\frac{(H^\circ-H_P)_T}{T_c}\right)_{N_2}$	C $\frac{B}{A}$	D log C	E $n = \frac{D}{\log 0.471}$
0.80	0.10	0.569	-	-		
0.85	0.10	0.464	0.358	0.773	-0.1118	0.158
0.90	0.10	0.371	0.316	0.853	-0.0691	0.098
0.95	0.10	0.300	0.284	0.945	-0.0246	0.035
0.85	0.25	1.412	-	-	-	-
0.90	0.25	1.065	0.806	0.757	-0.1209	0.171
0.95	0.25	0.843	0.648	0.770	-0.1135	0.160
1.00	0.25	0.711	0.545	0.766	-0.1158	0.164
1.10	0.25	0.506	0.418	0.828	-0.0820	0.116
1.20	0.25	0.394	0.347	0.881	-0.0550	0.078
0.95	0.50	2.085	-	-	-	-
1.00	0.50	1.604	1.278	0.796	-0.0991	0.140
1.10	0.50	1.089	0.932	0.857	-0.0670	0.095
1.20	0.50	0.805	0.758	0.943	-0.0250	0.035
1.00	0.75	2.910	2.070	0.712	-0.1475	0.209
1.10	0.75	1.785	1.513	0.850	-0.0706	0.100
1.20	0.75	1.277	1.191	0.935	-0.0292	0.041
1.00	1.00	7.46	-	-	-	-
1.10	1.00	2.57	2.139	0.833	-0.0794	0.112
1.20	1.00	1.785	1.646	0.923	-0.0348	0.049
1.10	1.25	3.51	2.885	0.823	-0.0846	0.119
1.20	1.25	2.335	2.125	0.913	-0.0395	0.056

Values of n obtained by plotting n for CO_2 and N_2 vs. T_R, and drawing a smooth curve

T_R	n
0.80	.52
0.85	.39
0.90	.28
0.95	.21
1.00	.16
1.10	.11
1.20	.04

Table 42. Calculation of $\frac{(H^{\circ}-H_P)_T}{\phi T_c}$

T_R	n	Carbon Dioxide: n log $\frac{304.19}{647.27}$	Carbon Dioxide: ϕ_{CO_2}	Nitrogen: n log $\frac{126.26}{647.27}$	Nitrogen: ϕ_{N_2}
0.80	0.52	-0.17	0.676	-0.366	0.441
0.85	0.39	-0.128	0.745	-0.276	0.530
0.90	0.28	-0.092	0.809	-0.198	0.631
0.95	0.21	-0.069	0.853	-0.148	0.711
1.00	0.16	-0.0523	0.886	-0.113	0.771
1.10	0.11	-0.036	0.920	-0.078	0.836
1.20	0.04	-0.013	0.970	-0.028	0.938

P_R	T_R	Carbon Dioxide: $\frac{(H^{\circ}-H_P)_T}{T_c}$	Carbon Dioxide: ϕ	Carbon Dioxide: $\frac{(H^{\circ}-H_P)_T}{\phi T_c}$	Nitrogen: $\frac{(H^{\circ}-H_P)_T}{T_c}$	Nitrogen: ϕ	Nitrogen: $\frac{(H^{\circ}-H_P)_T}{\phi T_c}$
0.10	0.80	0.394	0.676	0.582	-	-	-
0.10	0.85	0.292	0.745	0.39	0.358	0.530	0.676
0.10	0.90	0.213	0.809	0.26	0.316	0.631	0.501
0.10	0.95	-	-	-	0.284	0.711	0.400
0.25	0.85	0.993	0.745	1.33	-	-	-
0.25	0.90	0.812	0.809	1.005	0.806	0.631	1.278
0.25	0.95	0.690	0.853	0.810	0.648	0.711	0.912
0.50	0.95	1.629	0.853	1.910	-	-	-
0.596	0.95	-	-	-	1.742	0.711	2.45
0.25	1.00	0.608	0.886	0.688	0.545	0.771	0.707
0.50	1.00	1.305	0.886	1.472	1.282	0.771	1.66
0.596	1.00	-	-	-	1.426	0.771	1.85
0.75	1.00	2.370	0.886	2.68	2.082	0.771	2.70
0.25	1.10	0.490	0.920	0.532	0.418	0.836	0.50
0.50	1.10	1.018	0.920	1.11	0.932	0.836	1.115
0.596	1.10	-	-	-	1.096	0.836	1.314
0.75	1.10	1.600	0.920	1.74	1.513	0.836	1.810
1.00	1.10	2.305	0.920	2.51	2.148	0.836	2.56
1.25	1.10	3.258	0.920	3.54	2.885	0.836	3.45
0.25	1.20	0.407	0.970	0.42	0.347	0.938	0.37
0.50	1.20	0.839	0.970	0.865	0.758	0.938	0.81
0.596	1.20	-	-	-	0.893	0.938	0.953
0.75	1.20	1.300	0.970	1.34	1.191	0.938	1.27
1.00	1.20	1.775	0.970	1.83	1.655	0.938	1.77
1.25	1.20	2.265	0.970	2.34	2.125	0.938	2.27

Table 43. Calculation of T_o for C_6H_6
Linear Extrapolation of Joule-Thomson
Data of Lindsay and Brown (13)

Run	Pressure, psia		Temperature °F		$\frac{\Delta T}{\Delta P}$	$(\frac{\Delta T}{\Delta P})$ P low	T_o*	
	high	low	high	low			°F	°K
1	121	22	459	444	0.152	2.2	441.8	500.8
5	364	52	578	548	0.096	5.0	543.0	557.1
9	357	67	721	703	0.062	4.2	698.8	643.6
14	682	35	604	533	0.110	3.9	529.1	549.3
50	177	18	417	388	0.182	3.3	384.7	469.1
60	672	31	733	689	0.069	2.1	686.9	637.0

*$T_o = T \text{ low} - \frac{\Delta T}{\Delta P} \cdot P \text{ low}$

Table 44. Zero Pressure Specific Heat of C_6H_6 (41, 42)

T, °K	C_p^o, $\frac{cal}{g\text{-mole-}^oK}$
300	19.79
400	27.08
500	33.33
600	38.40
700	42.52
800	45.90
900	48.73

$$C_p^o = -8.06 + 0.10812T - 0.5104 \times 10^{-4}T^2 \ \frac{cal}{g\text{-mole-}^oK} \ (300\text{-}700\ ^oK) \qquad (23)$$

Comparison of Values from Equation 23 with Observed Values

T, °K	C_p^o (obs)	C_p^o (Eq. 23)	C_p^o (Ref. 3)	% Deviation (Eq. 23)	% Deviation (Ref. 13)
300	19.79	19.78	22.0	0.05	10.0
400	27.08	27.02		0.22	
500	33.33	33.24	32.4	0.27	2.5
600	38.40	38.44		0.11	
700	42.52	42.61	35.0	0.21	17.8
			Average	0.17	10.1

Table 45. Calculation of H for Isenthalps of Benzene

$$H^{o} = -8.06T + 0.05406T^{2} - 0.17013 \times 10^{-4}T^{3} \quad (23)$$

Run	T_o, °K	H $\frac{cal}{g\text{-mole}}$
1	500.8	7384.9
5	557.1	9345.7
9	643.6	12669.8
14	549.3	9064.4
50	469.1	6358.8
60	637.0	12404.2

Table 46. Calculation of T_o for n-Pentane by Linear Extrapolation of Joule-Thomson Data of Pattee and Brown (14)

Test	T high			T low			P high		P low		$\Delta T/\Delta P$	ΔT	T_o
	°F	°R	°K	°F	°R	°K	psia	atm	psia	atm	$\frac{°K}{atm}$	$\left(=\frac{\Delta T}{\Delta P}\cdot P\ low\right)$	°K
1	266	725.7	403.1	245	704.7	391.4	114	7.76	14	0.95	1.72	1.6	389.8
2	338	797.7	443.1	307	766.7	425.9	214	14.56	16	1.09	1.28	1.4	424.5
3	372	831.7	462.0	331	790.7	439.2	316	21.50	19	1.29	1.13	1.5	437.7
4	264	723.7	402.0	243	702.7	390.3	116	7.89	15	1.02	1.70	1.7	388.6
5	202	661.7	367.6	187	646.7	359.2	65	4.42	15	1.02	2.47	2.5	356.7
6	266	725.7	403.1	252	711.7	395.4	114	7.76	59	4.01	2.08	8.3	387.0

Table 47. Zero Pressure Specific Heat of $n\text{-}C_5H_{12}$ (40)

T, °K	C_p^o, $\frac{cal}{g\text{-}mole\text{-}°K}$
298.16	29.30
300	29.51
400	36.91
500	43.96
600	49.88

$$C_p^o = 3.65 + 0.09535T - 0.305 \times 10^{-4}T^2 \quad \frac{cal}{g\text{-}mole\text{-}°K} \qquad (20)$$

Deviation of Calculated from Observed Values for C_p^o

T, °K	C_p^o Calc. (Eq. 20)	C_p^o Obs.	% Deviation
300	29.51	29.51	0.00
400	36.91	36.91	0.00
500	43.70	43.96	0.60
600	49.88	49.88	0.00
		Average	0.15%

Integration of Equation of State for μ.--One way in which the enthalpy of a Joule-Thomson isenthalp may be identified is by extrapolating to zero pressure. Here, $H = H^{\circ}$, a function of T only. In order to carry out this extrapolation, an integral relation between T and P along the isenthalp may be obtained by integrating equation (2):

$$\mu C_p = T\left(\frac{\partial V}{\partial T}\right)_P - V \qquad (2)$$

For this purpose, we used the virial form of the equation of state, with two virial coefficients, thus:

$$C_p = T\left(\frac{dB}{dT}\right) - B \qquad (4)$$

$$C_p = C_p^{\circ} - T\int_{P_1}^{P_2}\left(\frac{\partial^2 V}{\partial T^2}\right)_P dP \qquad (34)$$

From (3),

$$C_p = C_p^{\circ} - T\int_{P_1}^{P_2}\left(\frac{d^2 B}{dT^2}\right) dP \qquad (35)$$

Since $$C_p^{\circ} = \alpha + \beta T + \gamma T^2 \qquad (12)$$

$$C_p = \alpha + \beta T + \gamma T^2 - T\int_{P_1}^{P_2}\left(\frac{d^2 B}{dT^2}\right) dP \qquad (36)$$

From equations (4) and (34),

$$\mu\left[\alpha + \beta T + \gamma T^2 - T\int_{P_1}^{P_2}\left(\frac{d^2 B}{dT^2}\right) dP\right] = T\left(\frac{dB}{dT}\right) - B \qquad (37)$$

Substituting $\mu = \left(\frac{\partial T}{\partial P}\right)_H$,

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{T\left(\frac{dB}{dT}\right) - B}{\alpha + \beta T + \gamma T^2 - T\int_{P_1}^{P_2}\left(\frac{d^2 B}{dT^2}\right) dP} \qquad (38)$$

When H is constant,

$$dT = \left[\frac{T\left(\frac{dB}{dT}\right) - B}{\alpha + \beta T + \gamma T^2 - T\int_{P_1}^{P_2}\left(\frac{d^2B}{dT^2}\right) dP}\right] dP \qquad (39)$$

The low pressure forms of the Beattie-Bridgeman and van der Waal's equations of state may be written as follows:

Beattie-Bridgeman: $$V = \frac{RT}{P} + \frac{B_1}{PV} \qquad (40)$$

van der Waals: $$V = \frac{RT}{P} + \left(b - \frac{a}{RT}\right) \qquad (41)$$

In equation (40) $$B_1 = RTB_o - A_o - \frac{Rc}{T^2} \qquad (42)$$

where B_o, A_o, and c are constants of the Beattie-Bridgeman equation of state. In equation (41), a and b are the constants of the van der Waals equation of state.

Differentiating equation (41), and substituting in equation (39):

$$dT = \left[\frac{2a - bRT}{\left(\alpha + \beta T + \gamma T^2 + \frac{2aP}{RT^2}\right) RT}\right] dP \qquad (43)$$

The corresponding equation, derived from equation (40) and (42), is:

$$dT = \left[\frac{-B_o + \frac{2A_o}{RT} + \frac{4c}{T^3}}{\alpha + \beta T + \gamma T^2 + \frac{P}{T}\left(\frac{2A_o}{RT} + \frac{Rc}{T^3}\right)}\right] dP \qquad (44)$$

Equations (43) and (44) can be gotten into the form MdP + NdT = 0 where $\left(\frac{\partial N}{\partial P}\right)_T = \left(\frac{\partial M}{\partial T}\right)_P$ so that equation (43) can be integrated to give

$$\frac{2aP}{T} - bRP - \alpha RT - \frac{\beta}{2} RT^2 - \frac{\gamma}{3} RT^3 = C_1 \qquad (45)$$

and equation (44) can be integrated to give

$$B_oP - \frac{2A_oP}{RT} - \frac{4cP}{T^3} + \alpha T + \frac{\beta}{2}T^2 + \frac{\gamma}{3}T^2 = C_2 \qquad (46)$$

C_1 and C_2 can be determined by setting P = 0, so that

$$C_1 = -\alpha RT_o - \frac{\beta}{2} RT_o^2 - \frac{\gamma}{3} RT_o^3 \qquad (47)$$

$$C_2 = \alpha T_o + \frac{\beta}{2} T_o^2 + \frac{\gamma}{3} T_o^3 \qquad (48)$$

By substituting for α, β, and γ the values from equation (17), and substituting P-T data along an isenthalp, the constants of the second virial coefficient may be defined. For example, if the temperature is read at three pressures along an isenthalp, and if these values are substituted in equation (45), three equations in three unknowns result. The unknowns are the constants of the second virial coefficient, a and b, and C_1. These equations can be solved simultaneously to give b and a. Similarly, by reading T at four different pressures along an isenthalp, and substituting these values into equation (46), four equations in four unknowns result, and these equations can be solved simultaneously to give the constants of the second virial coefficient for the Beattie-Bridgeman equation.

It should be remembered that these equations hold only when the pressure is sufficiently low.

Values of T have been read from CO_2 isenthalp II-5 at the four lowest recorded pressures, and the constants of the second virial coefficient have been determined for the Beattie-Bridgeman equation, as described above. These values are given in Table 48. They do not correspond to the known values of the constants in the range 0-100°C. Furthermore, the second virial coefficient calculated from these constants shows a negative temperature dependence. The values of the constants are, there-

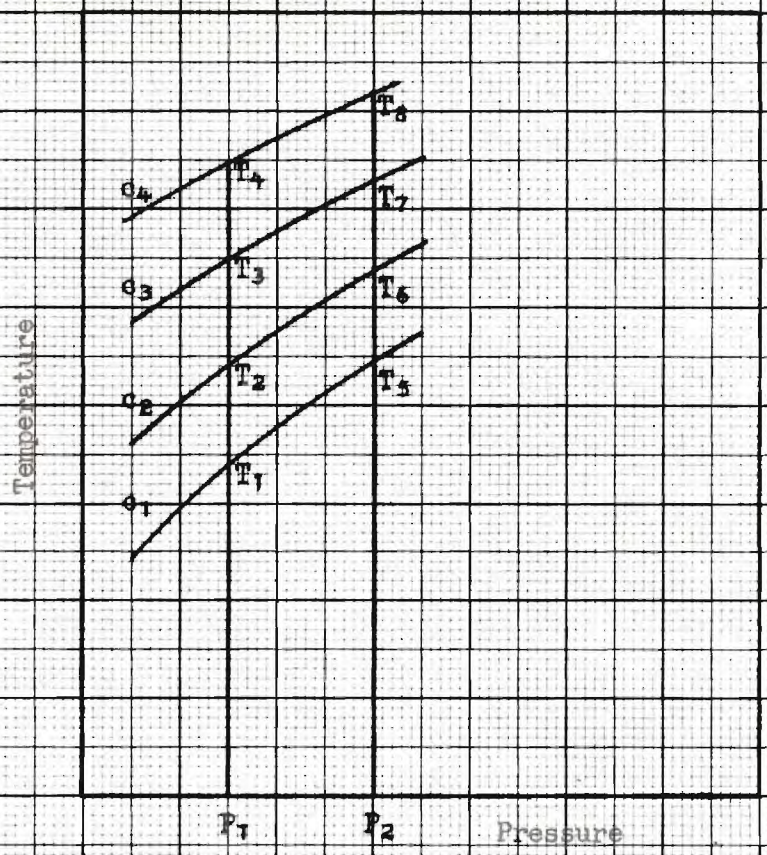

Figure 9. Calculation of the Second Virial Coefficient of CO_2

fore in error.

A second method was tried for solving equation (46) for the constants of the second virial coefficient. This consisted of reading the temperatures of four isenthalps at five atmospheres' pressure, and a 10 atmospheres. These equations can be solved as follows:

$$\int_{T_1}^{T_2}\left[B_o P_1 - \frac{2A_o P_1}{RT} - \frac{4cP_1}{T^3} + \alpha T + \frac{\beta}{2}T^2 + \frac{\gamma}{3}T^3\right] = c_2 - c_1 \qquad (49)$$

$$\int_{T_3}^{T_4}\left[B_o P_2 - \frac{2A_o P_2}{RT} - \frac{4cP_2}{T^3} + \alpha T + \frac{\beta}{2}T^2 + \frac{\gamma}{3}T^3\right] = c_4 - c_3 \qquad (50)$$

where c_1, c_2, c_3, and c_4 are the constants of integration of each isenthalp (fig. 9). Substitution of the temperature limits in these equations eliminates these constants of integration, and also eliminates B_o. This leaves two equations in two unknowns (A_o, c), and simultaneous solution yields the values of these constants. In order to determine B_o in this scheme, the values of A_o and c have to be substituted into equation (46) at several selected points along the isenthalp, and the average value of B_o is determined. All of these values of B_o, of course, should be identical, but due to lack of precision in the P-T data, the values vary.

This method was used on CO_2 isenthalps I-1, 3, 4, and 6, and the constants so calculated are shown in table 48. The values for the constants again fail to agree with the known values at 0 - 100°C, and again B shows a negative temperature dependence.

Both of these methods have been tried in other cases, and the results were always in error. The values of the constants always differed greatly from known values, and B always showed a negative

temperature dependence. The constants of the van der Waals equation were determined also. We conclude that B is very sensitive to the actual values of P and T used, and that the existing data for CO_2 probably either are not accurate enough, or do not extend to sufficiently low pressures to permit this kind of calculation.

The constants calculated as indicated above have been used to calculate T_o, the temperature of the isenthalp at P = 0, and the results are compared in table 49 with the results obtained from other methods. The results are in fair agreement. It is noted that T_R is above 1.0 in all four cases examined.

Table 48. Calculated Values for the Constants

of the Second Virial Coefficient of CO_2 for the Beattie-Bridgeman Equation

$$B_1 = RTB_o - A_o - \frac{Rc}{T^2} = B_o - \frac{A_o}{RT} - \frac{c}{T^3} \quad \frac{1}{\text{mole}}$$

Units used: l-atm, g-mole, ^oK

No.	B_o	A_o	C	Method
1	-49.33	-716.066	8.354×10^7	Isenthalp II-5 at 1.9, 3.8, 5.9, 9.2 Atm.
2	- 0.2894405	- 5.014868	3.611363×10^7	Isenthalp I-1, 3, 4, 6 at 5 and 10 Atm. B_o, average value from all four.
3	15.38211	323.7317	-26.49769×10^7	Isenthalp I-1 at 5, 10, 15, 20 Atm.
4	30.52359	-231.4374	114.229×10^7	Isenthalp I-3 at 5, 10, 15, 20 Atm.
5	133.3537	-1672.797	57.9012×10^7	Isenthalp I-4 at 5, 10, 15, 20 Atm.
6	-624.6479	-12717.6	282.7010×10^7	Isenthalp I-6 at 5, 10, 15, 20 Atm.
7	-1.157762	-5.014868	3.611663×10^6	Isenthalp I-1, 3, 4, 6 at 5 and 10 Atm. B_o, average value from all four.

Table 49. T_o for Some Isenthalps of CO_2

Isenthalp	No. 2 set of Constants	T_o, °K Linear Extrapolation	Lagrange Extrapolation	Beattie-Bridgeman Equation with Constants Determined by Beattie and Bridgeman (Ref. 33)
I-1	530.4	530.7	530.3	530.7
I-3	469.6	469.7	469.7	469.7
I-4	400.0	400.0	400.2	400.0
I-6	316.0	315.8	315.8	315.8

Temperature range of constants given by Beattie and Bridgeman is 273 - 373 °K. T_o given by these constants for Isenthalp I-6, therefore, is correct.

Table 50. Comparison of Calculated Values of the Second Virial Coefficient for CO_2 with Observed Values

(Values in Column 3 were calculated, using No. 2 set of constants for the Beattie-Bridgeman Equation (table 48).)

T, °K	B, $\frac{cc}{mole}$	
	Fig. 1	No. 2 Set
320	-105	-548.0
330	-100	-554.4
350	- 87	-571.7
375	- 75	-600.0
400	- 64	-633.8

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